STUDIES IN ELECTROCAPILLARITY.

by

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Thesis for the Degree of Doctor of Philosophy.

C O N T E N T S.

PART I.

THE ELECTROCAPILLARY CURVES OF ORGANIC ACIDS AND THEIR SALTS.

In the course of his extensive researches, Gouy examined the effect of many organic substances on the electrocapillary curve (Ann. Chim. Phys., 1906, 8, 291; 1906, 9, 75). He found that in solutions of inactive salts, such as sodium sulphate, neutral molecules give rise to a depression of the surface tension round about the maximum of the primitive curve, diminishing on both sides until, in many cases, the modified curve rejoins the primitive. Strong organic bases and their salts, on the other hand, give rise to a depression which is still large at the extreme right of the curve, at which the mercury has a relative negative potential. In a recent paper (Butler, Proc. Roy. Soc., A, 1929, 122, 399), the nature of these depressions has been analysed and it has been shown that the depressions produced by both classes of substances are governed by the same general equation;

$$\Delta\gamma = \Delta\gamma_0 \, e^{-aV^2+bV} \qquad \text{-------(1a)}$$

$$\Delta\gamma = \Delta\gamma_m \, e^{-a(V-V_m)^2} \qquad \text{------(1b)}$$

where $\Delta\gamma$ is the surface tension depression when the potential difference at the interface is V ; a and b are constants depending on the nature of the solution; $\Delta\gamma_m$ and V_m the maximum surface tension depression and the potential at which it occurs

and/

and $\Delta\gamma_o$ the surface tension lowering at zero potential difference, the precise position of which is unknown. It has further been shown that in a given solution the amount adsorbed is proportional to the surface tension lowering so that the latter can be used as a convenient measure of the variation of the amount of the adsorbed substance with the electric field. The curve of the surface tension depression plotted against the potential difference at the interface is termed the adsorption curve of the solution.

The equations given above apply equally to ions and neutral molecules, the effect of a positive charge being a displacement of the maximum depression (and adsorption) to the right (mercury negative) and a negative charge gives rise to a corresponding displacement on the left (positive) side.

TABLE I./

TABLE I.

Solution	V_m	Primitive
Tetra-methyl ammonium hydroxide M/10	1.47	Na_2SO_4, M/20
Tetra-methyl ammonium hydroxide, M/10;H_2SO_4,M/20	1.42	Na_2SO_4, M/20
Tetra-ethylammonium hydroxide, M/10	1.27	Na_2SO_4, M/20
Tetra-ethylammonium hydroxide, M/10; H_2SO_4,M/20	1.24	Na_2SO_4, M/20
Tri-ethyl sulphine hydroxide, M/10	1.36	Na_2SO_4, M/20
Tri-ethyl sulphine hydroxide,M/10; H_2SO_4, M/20	1.37	Na_2SO_4, M/20
Choline, M/10	1.47	Na_2SO_4, M/20
Choline, M/10; H_2SO_4,M/20	1.45	Na_2SO_4, M/20
Tri-ethylamine, M/10	0.62	Na_2SO_4, M/20
Tri-ethylamine,M/10;H_2SO_4,M/20	1.25	Na_2SO_4, M/20
Tri-ethylamine,M/10;H_2PO_4,M	1.3	H_3PO_4, M
Iso-amylamine, M/10	0.62	Na_2SO_4, M/20
Iso-amylamine,M/10; H_2SO_4,M/20	1.07	Na_2SO_4, M/20
Iso-amylamine,M/10; H_3PO_4,M	Ca 1.2	H_3PO_4, M
Benzylamine,sat,; Na_2SO_4,M/2	0.58	Na_2SO_4, M/2
Benzylamine,M/10;H_2SO_4, M/20; Na_2SO_4,M/2	0.72	Na_2SO_4, M/2
p-Toluidine,sat,; Na_2SO_4,M/2	0.50	Na_2SO_4, M/2
p-Toluidine,M/100,H_2SO_4,M/2	0.82	H_2SO_4, M/2
Pyridine,M/10; Na_2SO_4, M/2	0.71	Na_2SO_4, M/2
Pyridine,M/10; H_2SO_4,M/20;Na_2SO_4,M/2	1.22	Na_2SO_4, M/2
Caffein,M/100, Na_2SO_4, M/2	0.55	Na_2SO_4, M/2
Caffein,M/100; H_2SO_4, M/2	0.67	H_2SO_4, M/2

Table I gives the potential differences, measured against the normal calomel electrode,* at which the maximum surface tension depressions occur with a number of organic bases and their salts, according to Gouy's data. It can be seen that strong bases and their salts, in which the active material is present entirely as the cation, give maximum depressions at -1.3 to -1.5 volts. Weak bases, which are only slightly dissociated, give maximum depressions in the vicinity of the maximum of the primitive curve (- 0.49 volts) and the maxima of their salts, which contain the ions in greater proportion, show a considerable displacement to the negative side. The fact that the maxima of salts of weak bases occur at less negative potentials than those of the strong bases is probably due to partial hydrolysis of the former. In a few cases in which data is available the addition of an excess of a strong acid, which must reduce the extent of hydrolysis, causes a further shift to the negative side. Caffein, an extremely weak base ($K_b = 4 \times 10^{-14}$) which is present largely as unionised molecules even in relatively acid solutions, gives a maximum in M/2 sulphuric acid at nearly the same p.d. as in sodium sulphate.

No/

* Gouy's used as standard electrode, Hg Hg_2SO_4, Na_2SO_4 M/2. The electrode potentials on this scale are 0.38 volts higher than the corresponding values referred to the normal calomel electrode.

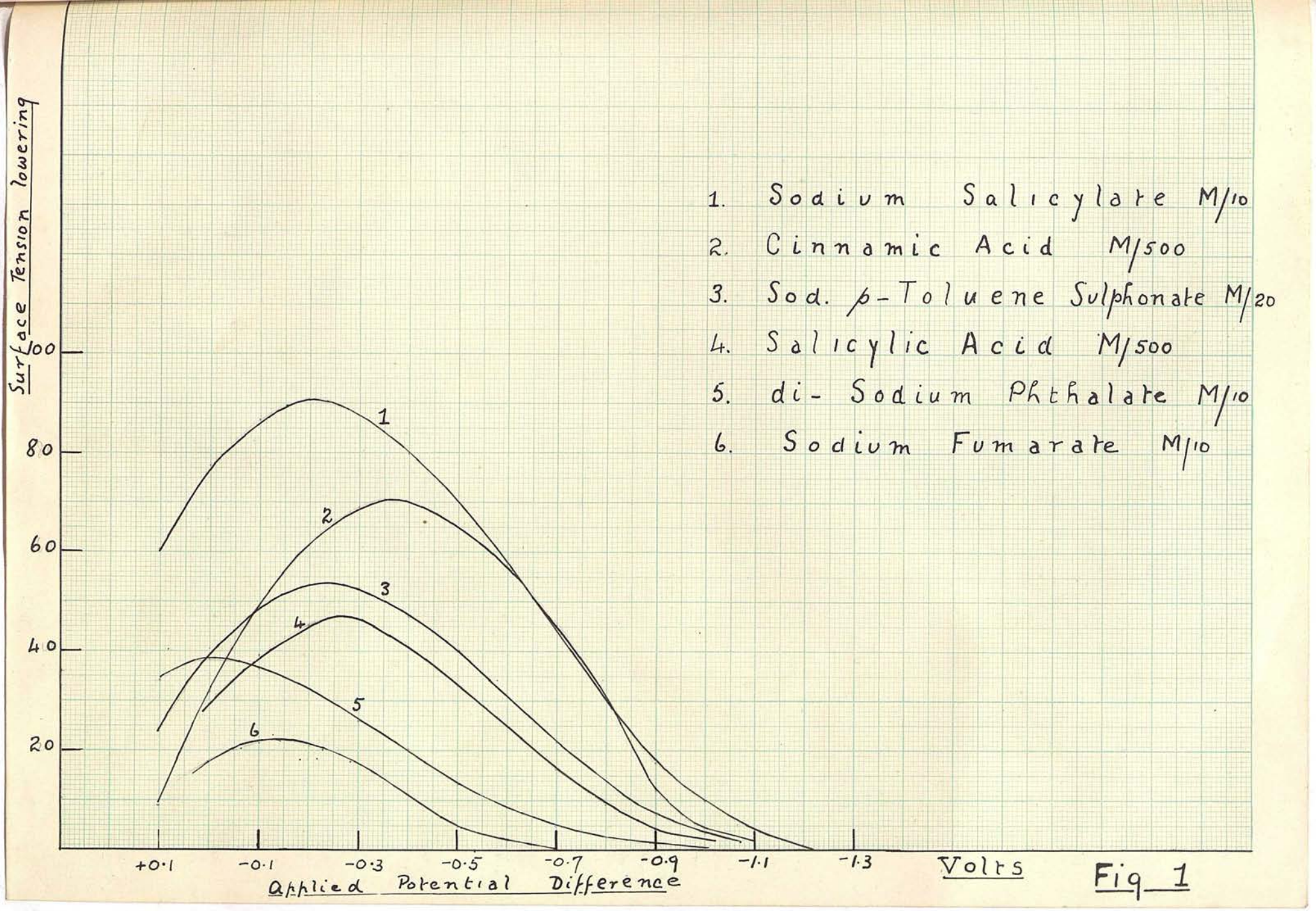
Surface Tension lowering
100
80
60
40
20
1
2
3
4
5
6
+0·1
-0·1
-0·3
-0·5
-0·7
-0·9
-1·1
-1·3
Volts
Applied Potential Difference
1. Sodium Salicylate M/10
2. Cinnamic Acid M/500
3. Sod. p-Toluene Sulphonate M/20
4. Salicylic Acid M/500
5. di- Sodium Phthalate M/10
6. Sodium Fumarate M/10

Fig 1

No measurements were made by Gouy of solutions containing salts of weak acids or of strong organic acids themselves. We have therefore determined the electrocapillary curves of a number of typical acids and their salts, to ascertain if the position of maximum adsorption of their anions is displaced towards positive potentials. The main characteristics of the curves obtained are summed up in Table II, and Fig.1 shows a few typical adsorption curves. V_m is the potential difference at the mercury-solution interface, relative to the normal calomel electrode, at which the maximum surface tension lowering $\Delta\gamma_m$ occurs and a the approximate value of the constant in equation (1). The solutions in every case were half-molar with respect to sodium sulphate. Owing to the very different solubilities of the organic acids and their salts and to the fact that salts have a much smaller surface activity than the acids at the same concentrations, it was not convenient to determine their curves at equivalent concentrations. The effect of concentration on the position of the maximum and on the form of the curve is however small.

TABLE II./

TABLE II.

Characteristics of electrocapillary curves of organic acids and their salts in M/2 sodium sulphate.

	Acids				Sodium Salts			
	Concentration	$-V_m$	m	a	Concentration	$-V_m$	m	a
Benzoic	M/100	0.40	59.7		M/10	0.22	54.3	1.9
					M/100	0.23	31.3	2.0
Salicylic	M/500	0.30	64.7	3.0	M/10	0.21	89.4	1.3
					M/20	0.23	80.7	1.5
Cinnamic	M/500	0.35	69.1	2.2	M/10	0.30	87.1	1.01
o-Toluic	M/500	0.37	44.9	-	M/10	0.27	52.6	1.9
m-Toluic	M/500	0.39	52.7	-	M/10	0.24	68.2	1.3
p-Toluic	sat. (M/500)	0.32	51.4	-	M/10	0.29	69.6	1.5
Phthalic	M/100	0.29	46.0	2.0	M/10[1]	0.29	77.3	1.3
					M/10[2]	0.01	38.8	2.0
					M/20[2]	0.03	31.9	2.0
Terephthalic	-	-	-	-	M/10[2]	0.14	60.8	2.3
Trichloracetic	M/10	0.27	25.0	2.6	M/10	0.22	18.6	2.5
					M/20	0.24	16.9	-
Benzene sulphonic	-	-	-	-	M/10[3]	0.28	56.0	2.4
					M/20[3]	0.28	45.3	2.4
p-Toluene sulphonic	M/10	0.27	62.9	1.9	M/10	0.27	62.9	1.9
	M/20	0.26	53.8	2.2				
Fumaric	M	0.29	38.0		M/10[2]	0.13	22.1	4.4
Maleic	M/10	0.32	35.5	2.3	M/10[2]	0.25	11.2	

[1] Mono-sodium salt. [2] Di-sodium salts. [3] Potassium salt.

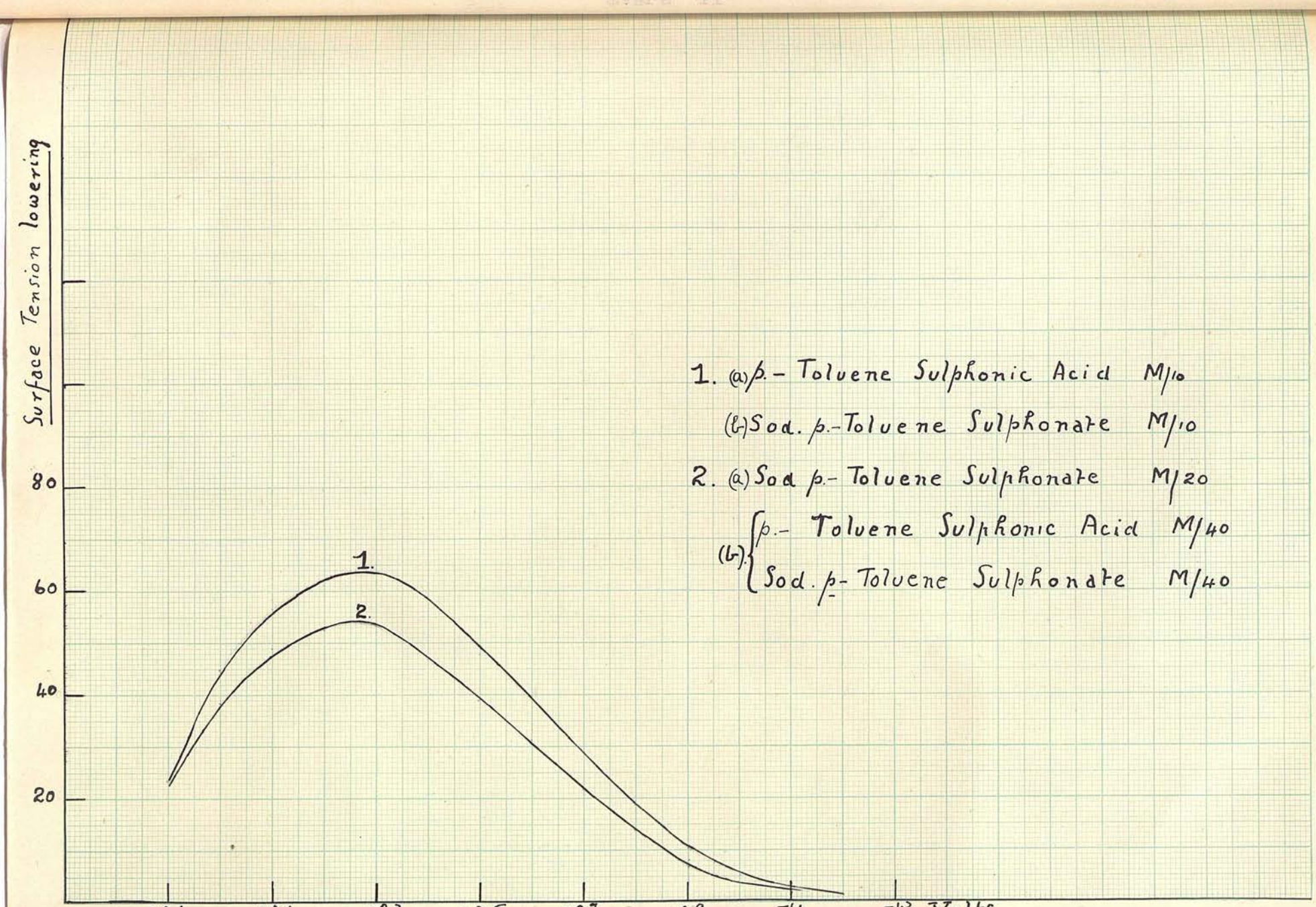
Surface Tension lowering
80
60
40
20
1.
2.
+0·1
-0·1
-0·3
-0·5
-0·7
-0·9
-1·1
-1·3
Volts
Applied Potential Difference
1. (a) p.- Toluene Sulphonic Acid M/10
(b) Sod. p.- Toluene Sulphonate M/10
2. (a) Sod p.- Toluene Sulphonate M/20
(b) p.- Toluene Sulphonic Acid M/40
Sod. p.- Toluene Sulphonate M/40

Fig. 2

It is evident that the displacements of the curves of organic acids and their salts to the positive side are small compared with those of the bases to the negative. The weak acids show maximum depressions at -0.3 to -0.4 volts and their salts at potentials only about 0.1 volt more negative. That this behaviour cannot be ascribed to hydrolysis of the salts, although this may be a contributary factor in some cases, is shown by the fact that p-toluene sulphonic acid and its sodium salt give maxima in the same region and also mixtures of the two to the same total concentration give identical curves. (Fig.2)
The only salts investigated which showed larger displacements were the di-sodium salts of phthalic, terephthalic and fumaric acids. It thus appears that two negative charges must be carried by the anion before any considerable displacement of the adsorption curve occurs.

In order to ascertain whether the small degree of hydrolysis which occurs in solutions of the salts of weak acids can have any appreciable influence on the curves, measurements were made of a number of mixtures of benzoic acid and sodium benzoate.
Fig.3 shows the effect of adding sodium benzoate to a solution of benzoic acid. The effect of sodium benzoate even in relatively large amounts on the position/

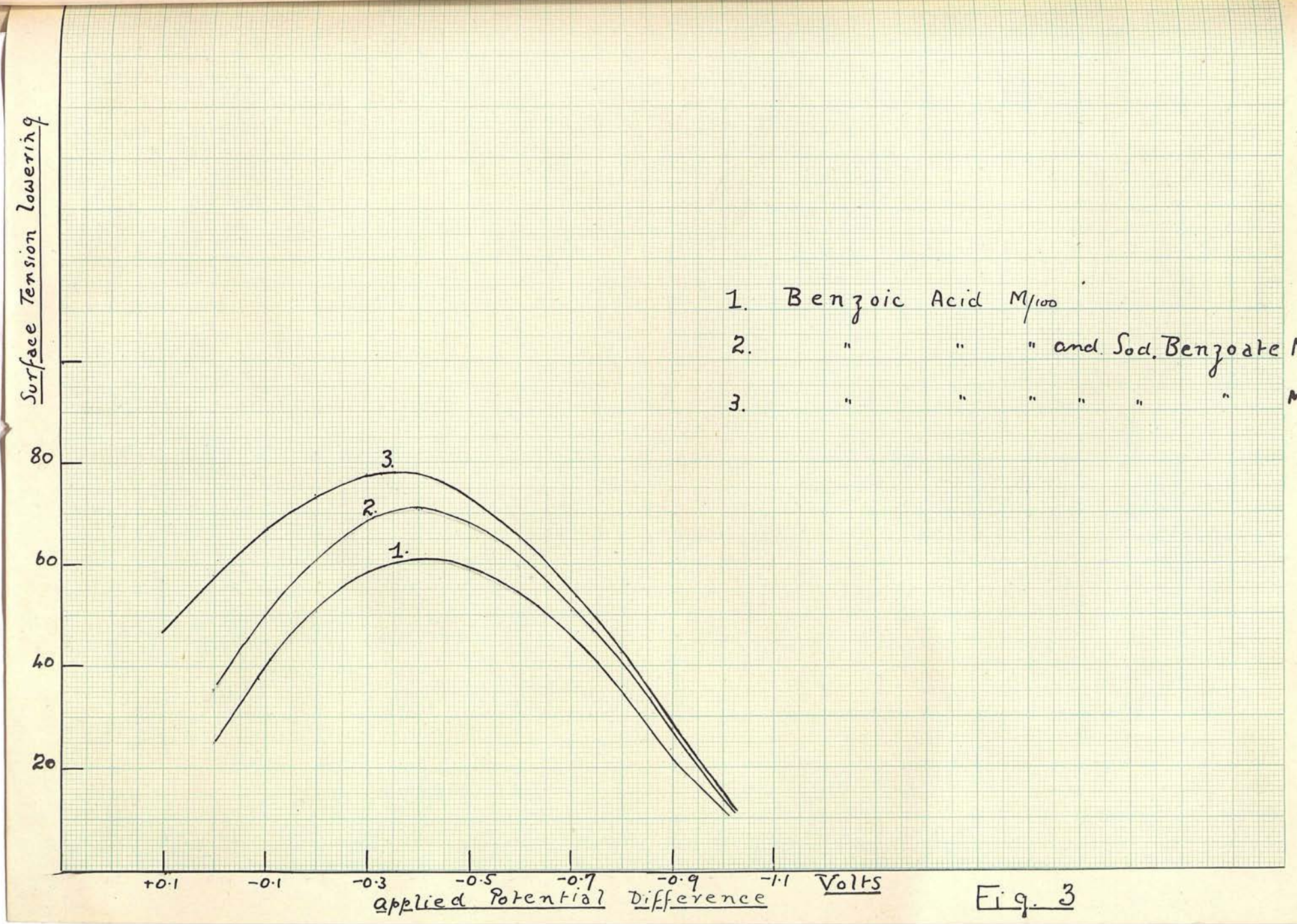
Surface Tension lowering
80
60
40
20
3.
2.
1.
+0·1
-0·1
-0·3
-0·5
-0·7
-0·9
-1·1
Volts
Applied Potential Difference
1. Benzoic Acid M/100
2. " " " and Sod. Benzoate M/100
3. " " " " " " M/10

Fig. 3

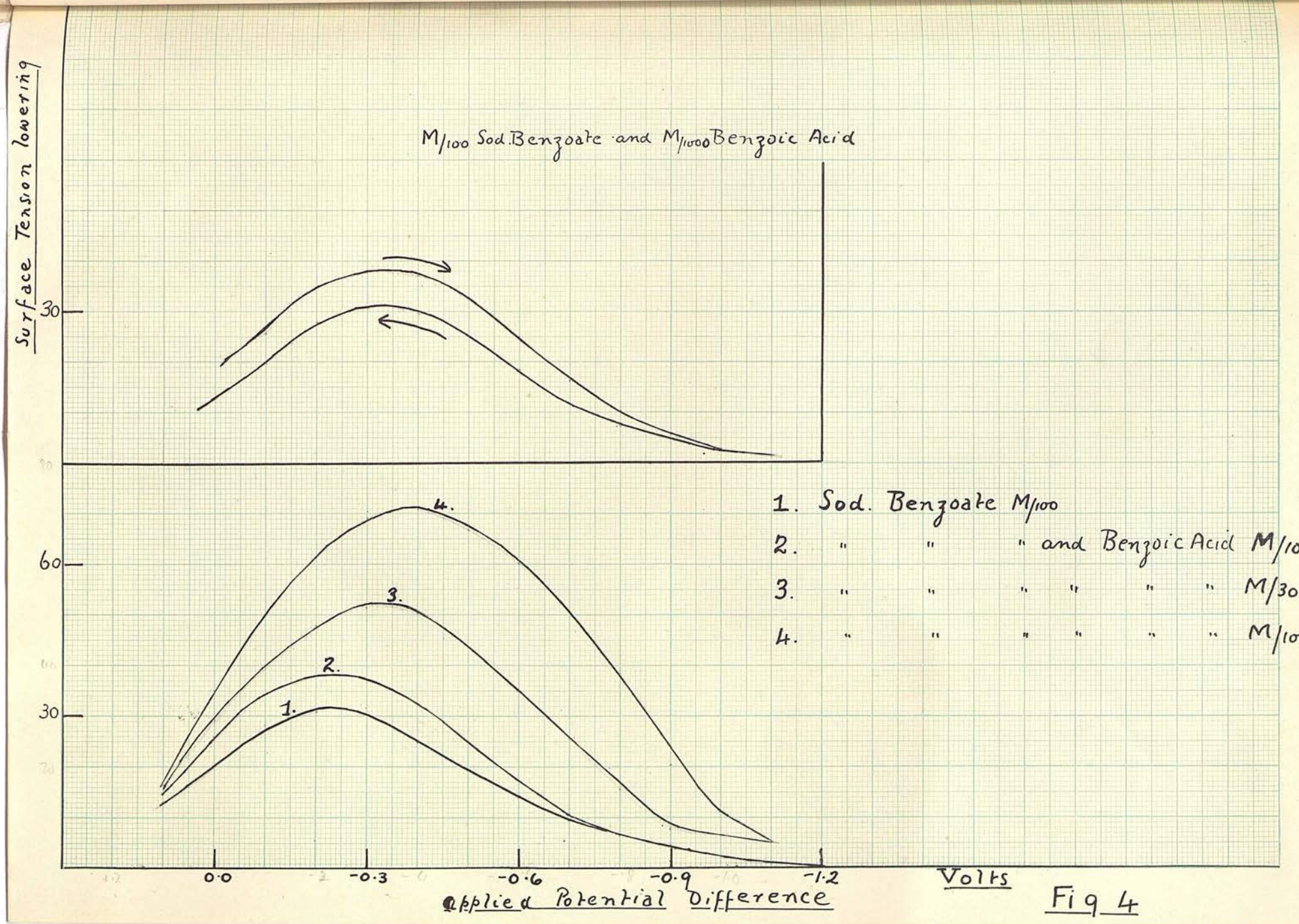
Surface Tension lowering
M/100 Sod. Benzoate and M/1000 Benzoic Acid
30
60
30
1.
2.
3.
4.
1. Sod. Benzoate M/100
2. " " " and Benzoic Acid M/1000
3. " " " " " " M/300
4. " " " " " " M/100
0·0
-0·3
-0·6
-0·9
-1·2
Volts
Applied Potential Difference

Fig 4

position of the maximum is slight and the small amounts of benzoate ion due to the natural dissociation of benzoic acid can have no appreciable effect on the curve. The electrocapillary curve of M/100 benzoic acid was also determined in M/2 sulphuric acid, which must reduce the ionisation to a very small degree, and was found to be nearly identical with that in sodium sulphate.

In Fig.4 are shown the curves of sodium benzoate solutions containing varying amounts of benzoic acid. Benzoic acid, being much more active than its salt, has a very large effect on the maximum depression. But the position of the maximum could scarcely be affected by the small concentrations of acid present in sodium benzoate solutions owing to hydrolysis.

It appears then that the difference between the behaviour of acids and bases cannot be accounted for as due to hydrolysis of the salt or dissociation of the acid. It appears probable that conditions at the interface differ on the positive and negative branches of the primitive curve. It has been observed (Butler, loc.cit.) that the adsorption curves of most substances are steeper on the left than on the right side. The more rapid fall off of adsorption on the left may be due to a more rapid rate of increase of the electric field with the applied potential region on the/

the positive side of the primitive maximum. It has been shown by Bowden and Rideal (Proc. Roy. Soc., A, 1928, 120, 59) that at potentials more negative than about 0.7 volts (the equilibrium potential of the hydrogen electrode in these solutions), the polarisation is due to the liberation of hydrogen. At less negative potentials oxygen appears at the interface and the field strength may vary at a greater rate with the potential difference. It is also possible that the liberated oxygen displaces the adsorbed material to a certain extent.

Electrocapillary viscosity.

As Gouy observed, the solutions of the acids exhibit considerable "electrocapillary viscosity", i.e. the surface tension continues to change for a considerable time after an alteration in the polarising potential has been made. We have made some observations which appear to throw light on the nature of this effect. When the electrocapillary curves of benzoic acid and benzoic acid-sodium benzoate mixtures are taken rapidly, the mercury surface being unchanged, the surface tension depressions observed with increasing (negative) polarisation are greater than those taken with decreasing polarisation (Fig.4 inset). With/

With a solution containing M/100 sodium benzoate and M/1000 benzoic acid, the curve obtained with decreasing polarisation was identical with that of M/100 sodium benzoate. In this case, it appears that no benzoic acid is present at the interface when the mercury is first strongly negatively polarised. Now in the negative polarisation of mercury, hydrogen ions are discharged and the corresponding amount of hydroxyl ions remain in solution. These will be sufficient to cause the ionisation of the small amount of benzoic acid present. In benzoic acid solutions and in mixtures containing a larger concentration of benzoic acid, the alkalinity produced by hydrolysis will cause some increase in the amount of benzoate ion present and a corresponding decrease in the amount of undissociated benzoic acid, with a consequent decrease in the surface tension lowering. With increasing polarisation, only a very minute discharge of hydrogen ions occurs at the low polarisations at which the adsorption occurs. The surface tension depression observed when the measurements are carried out slowly, i.e. when the polarising potential is kept constant at each value until the surface tension reaches a steady value, are usually not far different from those obtained rapidly with increasing polarisation. When ample time is given to each reading, it may/

may be expected that in most cases, the acidity at the interface will finally be determined by the concentrations of acid and salt in the solution.

Experimental.

The electrocapillary curves were determined by an apparatus similar to that of S.W.J. Smith (Phil. Trans., A, 1899, 193, 48) by measuring the height of the mercury column required to bring the miniscus in a fine capillary tube to the same position at each value of the applied potential difference. The standard electrode was a normal calomel electrode and the potential difference between this and the mercury in the capillary was varied in steps of 0.1 volt by means of a potential divider (10000 ohms in 20 coils of 500 ohms each). The measurements were carried out at room temperature (10 - 15°), since it was found that 10° difference of temperature had no appreciable effect, probably owing to a compensation of factors.

The acids were purified by several recrystallisations from suitable solvents or, in certain cases, by repeated sublimation, until they had a constant melting point. The solutions were made up to the stated concentration with respect to both sodium sulphate and the organic substance. The salts were prepared in solution by adding the calculated amount of/

of a standardised carbon dioxide-free sodium hydroxide solution to the acid before adjusting the volume.

The measurements, as given in Table III are reduced to Gouy's standard i.e. the maximum surface tension between mercury and pure water is taken as 1000 (maximum in M/2 Na_2SO_4, 1001). The characteristics of the capillary changed somewhat with use, causing a slight modification of the primitive curve. This curve was determined at frequent intervals during the experiments. The significant variations are given in curves A and B (Table III) and under the readings of each solution is stated the primitive curve with which they are to be compared.

TABLE III.

Electrocapillary curves of organic acids and salts in M/2 Sodium Sulphate,

V	Sodium Sulphate M/2 (A)	Sodium Sulphate M/2 (B)	Benzoic Acid M/100	Salicylic Acid M/500	Cinnamic Acid M/500
+ 0.4	-	-	-	-	-
+ 0.3	-	-	-	-	-
+ 0.2	-	-	-	-	-
+ 0.1	865.4	855.7	859.5	856.0	857.3
- 0.0	911.7	907.5	887.1	883.2	883.2
- 0.1	946.5	944.7	908.4	907.6	898.8
- 0.2	972.0	971.8	923.5	928.1	911.9
- 0.3	991.3	991.0	933.6	944.6	923.2
- 0.4	998.7	999.2	941.0	958.6	930.5
- 0.5	1000.4	1000.4	942.9	967.3	936.0
- 0.6	997.4	996.8	945.5	970.7	940.8
- 0.7	987.7	987.0	943.0	970.3	942.7
- 0.8	972.2	971.7	937.9	966.2	942.7
- 0.9	953.1	951.7	928.1	949.2	941.7
- 1.0	930.7	928.6	920.4	927.2	925.9
- 1.1	901.7	901.4	898.7	900.5	899.3
- 1.2	872.1	870.3	870.2	870.2	869.1
- 1.3	837.2	835.5	836.3	835.8	836.0
- 1.4	798.6	796.8	798.2	798.0	798.6
- 1.5	756.1	753.4	756.6	755.2	755.9
- 1.6	708.5	706.6	709.3	708.1	708.7
- 1.7	657.9	656.5	658.5	657.8	658.3
- 1.8	603.4	600.4	603.4	603.0	602.6
			A	A	A

V.	O-Toluic acid M/500	m-Toluic Acid M/500	p-Toluic acid satd.	Trichloracetic acid M/10
+ 0.4	-	-	-	-
+ 0.3	-	-	-	-
+ 0.2	-	-	-	-
+ 0.1	862.7	860.6	860.8	858.2
0.0	902.6	896.8	896.8	895.8
- 0.1	927.0	917.3	917.7	925.7
- 0.2	941.4	931.3	931.1	948.5
- 0.3	950.7	941.3	939.8	967.0
- 0.4	956.7	947.7	949.2	979.7
- 0.5	964.4	952.2	956.8	986.1
- 0.6	968.3	952.5	960.3	985.8
- 0.7	972.3	954.7	960.5	979.9
- 0.8	968.3	955.0	967.8	968.1
- 0.9	949.9	947.8	949.3	950.6
- 1.0	927.3	925.7	925.6	927.9
- 1.1	898.9	900.5	898.5	901.3
- 1.2	870.0	869.9	869.5	871.9
- 1.3	835.9	836.3	835.2	837.5
- 1.4	798.0	798.4	798.0	798.7
- 1.5	755.8	755.5	755.7	757.6
- 1.6	708.8	708.1	708.1	710.5
- 1.7	657.8	657.4	656.9	659.8
- 1.8	603.4	602.6	602.4	603.4
	A	A	A	A

V.	Maleic acid M/10	p-Toluene Sulphonic acid M/10	Sodium p-Toluene sulphonate M/10	p-Toluene sulphonic acid M/20
+ 0.4	-	657.7	-	651.6
+ 0.3	745.8	744.2	-	744.6
+ 0.2	810.4	795.8	796.0	802.4
+ 0.1	860.7	832.7	832.1	841.3
0.0	895.9	863.6	864.2	873.8
- 0.1	921.1	889.1	889.1	898.4
- 0.2	940.5	911.4	910.8	920.2
- 0.3	956.1	928.2	928.2	938.9
- 0.4	964.7	942.3	941.9	952.6
- 0.5	970.3	953.6	953.8	962.0
- 0.6	971.3	957.6	957.8	966.9
- 0.7	968.5	958.5	958.7	966.2
- 0.8	963.4	953.6	953.8	958.6
- 0.9	947.8	941.0	940.9	945.7
- 1.0	927.3	923.4	922.8	925.7
- 1.1	900.6	898.6	898.4	900.4
- 1.2	872.0	868.5	868.1	870.4
- 1.3	838.9	835.9	833.9	835.5
- 1.4	798.6	796.7	795.8	797.0
- 1.5	756.3	754.4	753.2	754.9
- 1.6	709.0	708.4	706.9	708.5
- 1.7	659.0	658.0	655.4	658.0
- 1.8	603.1	603.0	600.5	603.0
	A	B	B	B

V.	Sodium Benzoate M/10	Sodium Benzoate M/100	Sodium Cinnamate M/10	Sodium Salicylate M/10	Sodium Salicylate M/20
+ 0.4	-	-	-	-	-
+ 0.3	-	-	-	-	-
+ 0.2	-	-	-	751.7	-
+ 0.1	833.3	852.5	-	796.2	805.6
0.0	863.4	891.3	836.9	831.2	839.9
- 0.1	892.8	918.0	863.9	860.8	867.3
- 0.2	917.9	941.7	887.0	882.8	901.3
- 0.3	937.0	961.0	904.1	904.8	911.5
- 0.4	950.7	974.2	915.3	921.2	927.4
- 0.5	962.5	982.1	923.2	932.6	938.8
- 0.6	967.4	983.7	926.7	940.1	946.3
- 0.7	965.5	978.1	926.7	944.3	949.2
- 0.8	958.0	965.5	922.2	941.9	946.4
- 0.9	944.8	948.7	918.8	934.4	937.1
- 1.0	925.7	926.1	908.9	919.2	919.7
- 1.1	900.7	901.5	889.9	897.9	896.7
- 1.2	871.2	870.8	866.5	870.1	867.1
- 1.3	836.0	835.2	834.5	835.8	861.3
- 1.4	796.8	798.1	796.2	797.2	795.6
- 1.5	754.1	755.6	752.7	754.4	752.6
- 1.6	707.4	708.5	706.8	706.6	705.9
- 1.7	656.3	657.7	635.8	655.6	654.8
- 1.8	600.4	602.5	600.6	600.5	597.9
	B	B	B	B	B

V	Sodium o-toluate M/10	Sodium m-toluate M/10	Sodium p-toluate M/10	Sodium hydrogen phthalate M/10	di-Sodium phthalate M/10	di-Sodium phthalate M/20
+ 0.4	-	-	-	-	-	-
+ 0.3	-	-	-	-	-	-
+ 0.2	-	-	-	770.2	-	-
+ 0.1	834.2	-	812.3	821.8	822.1	821.1
0.0	868.7	853.6	853.9	854.4	869.6	876.9
- 0.1	898.2	882.9	881.9	880.0	909.4	914.0
- 0.2	920.7	904.5	904.4	899.2	939.8	942.7
- 0.3	938.7	923.7	921.8	914.0	964.4	965.4
- 0.4	950.8	937.0	934.0	926.2	980.0	980.9
- 0.5	959.3	946.8	940.9	934.0	988.0	989.1
- 0.6	961.9	950.7	944.8	938.4	988.8	989.3
- 0.7	961.9	950.7	945.8	940.5	981.1	984.7
- 0.8	955.7	943.9	941.8	937.6	969.2	969.2
- 0.9	943.0	934.9	935.0	930.8	950.6	950.1
- 1.0	924.5	919.8	921.2	917.9	928.2	927.2
- 1.1	899.0	897.9	897.0	897.7	900.2	900.3
- 1.2	870.4	868.8	870.4	869.3	869.8	868.8
- 1.3	835.9	836.4	835.2	836.8	835.8	834.7
- 1.4	798.0	797.7	796.6	797.9	796.8	796.1
- 1.5	754.6	754.6	753.5	755.3	754.2	753.6
- 1.6	707.2	707.0	707.4	708.5	706.4	706.3
- 1.7	656.8	656.3	656.0	657.5	654.5	655.3
- 1.8	600.9	600.7	601.0	602.2	599.2	600.7
	B	B	B	B	B	B

V	Sodium terephthalate M/10	Sodium trichloracetate M/10	Sodium trichloracetate M/20	Potassium benzene sulphonate M/10	Potassium benzene sulphonate M/20
+ 0.4	-	-	-	-	-
+ 0.3	-	-	-	-	-
+ 0.2	-	-	-	-	-
+ 0.1	-	-	862.4	836.9	849.1
0.0	842.8	-	902.0	871.1	883.2
- 0.1	884.5	929.7	932.1	897.4	908.4
- 0.2	912.5	953.8	956.7	918.5	930.4
- 0.3	934.3	973.3	974.4	935.0	946.2
- 0.4	953.0	985.1	986.1	949.7	957.5
- 0.5	967.1	990.9	991.8	960.2	966.3
- 0.6	973.2	989.6	991.6	964.8	971.8
- 0.7	972.7	982.1	984.2	964.2	971.6
- 0.8	963.4	968.5	970.1	958.8	964.9
- 0.9	947.8	951.1	952.1	944.8	949.1
- 1.0	926.4	928.2	928.9	924.9	927.7
- 1.1	899.8	-	901.8	898.5	900.2
- 1.2	868.2	-	871.6	869.2	870.9
- 1.3	835.8	-	837.2	835.7	835.1
- 1.4	797.0	-	798.6	796.8	797.4
- 1.5	756.2	-	756.1	754.5	755.2
- 1.6	710.5	-	709.1	708.4	708.3
- 1.7	-	-	658.2	656.5	656.9
- 1.8	-	-	603.8	602.4	602.4
	B	A	A	B	B

V	Sodium Maleate M/10	Sodium fumarate M/10
+ 0.4	-	-
+ 0.3	-	-
+ 0.2	-	-
+ 0.1	-	-
0.0	902.1	889.8
- 0.1	937.5	923.8
- 0.2	961.3	950.9
- 0.3	980.1	973.5
- 0.4	992.2	989.7
- 0.5	996.7	995.0
- 0.6	995.7	995.3
- 0.7	987.4	987.8
- 0.8	972.2	972.9
- 0.9	953.1	953.6
- 1.0	929.9	929.8
- 1.1	900.0	902.6
- 1.2	871.4	870.2
- 1.3	835.8	835.3
- 1.4	798.1	757.2
- 1.5	755.5	754.3
- 1.6	708.4	707.5
- 1.7	657.0	657.2
- 1.8	601.4	600.6
	B	B

SUMMARY.

1. The electrocapillary curves of a number of organic acids and their salts have been determined in M/2 sodium sulphate. The maximum adsorption of salts of weak acids occurs at potential differences about 0.1 volt more positive than those of the acids themselves, and strong acids give maxima in the same region. The displacement of the potential of maximum adsorption of organic anions towards positive potentials, is thus much less than the corresponding displacement towards negative potentials observed with organic cations.

2. A study of mixtures of benzoic acid and sodium benzoate shows that this behaviour cannot be due to hydrolysis of the salts. It is suggested that the conditions under which adsorption occurs must differ on the positive and negative branches of the electrocapillary curve.

3. The electrocapillary viscosity exhibited by solutions of the acids, appears to be due to the formation of alkali in the solution, owing to discharge of hydrogen ions at the mercury surface.

P A R T II.

SELECTIVE ADSORPTION IN SOLUTIONS CONTAINING TWO ACTIVE SUBSTANCES.

The surface tensions of solutions of two or more active substances have not been widely investigated. Morgan and McKirahan (J. Amer. Chem. Soc., 1913, 35, 1750) determined a few cases of mixtures of salts of organic acids and found that if the surface tension lowerings produced by the two salts separately were not far removed from water, that of the mixture is nearly equal to their sum. If, however, one of the solutes causes a much greater lowering than the other, the value for the mixture is nearer to the one with the greater lowering, an observation which is supported by the measurements of Strebnitzki (J. Russ. Phys. Chem. Soc., 44, 145). Szyszkowski (Z. physikal. Chem., 1908, 64, 385) also found that in a mixture of isovaleric acid and its barium salt, the lowering produced by the former being much greater than that of the latter, the surface tension lowering is to be attributed to the undissociated part of the acid. In experiments with two mixtures of fatty acids, he found that the surface tension lowerings were an additive property of those of the components.

According to the thermodynamical principles of Gibbs, the surface energy at an interface tends to a minimum. If a substance is present in a solution which lowers its interfacial tension, it will be present/

present at the interface in greater amount than in the bulk of the solution. In a solution containing two active substances we might expect that which causes the greatest surface tension lowering to be adsorbed to the greatest extent. It is easy to see that under certain circumstances one component may be exclusively adsorbed. Consider a solution of a substance A, which causes a greater surface tension lowering (in equivalent concentration) than a substance B. If we add B to this solution it is possible that the conditions may be such that the surface energy is not lowered by its adsorption, since this might involve the displacement of some of the more active substance A. Under these conditions we should get the exclusive adsorption of A.

The use of the mercury-solution interface instead of the air-solution interface has the advantages that the potential difference between the mercury and the solution may be varied by polarisation and the effect of change of the electrical conditions on the behaviour of the mixture may be observed. We have determined the electrocapillary curves of solutions of a number of mixtures of active substances in M/2 sodium sulphate. Their behaviour is summarised below.

A/

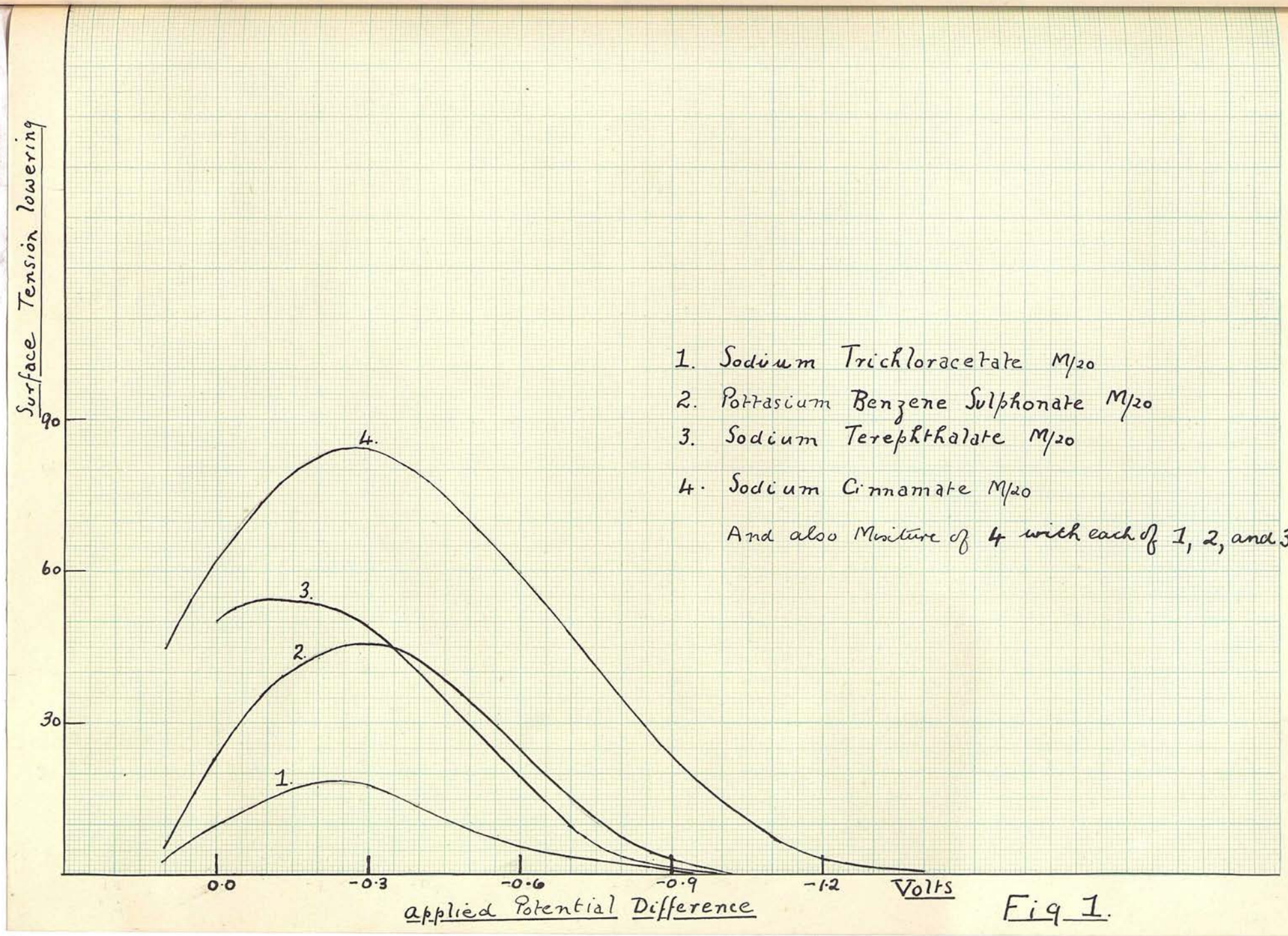
Surface Tension lowering
90
60
30
4.
3.
2.
1.
0·0
-0·3
-0·6
-0·9
-1·2
Volts
applied Potential Difference
1. Sodium Trichloracetate M/20
2. Potassium Benzene Sulphonate M/20
3. Sodium Terephthalate M/20
4. Sodium Cinnamate M/20
And also Mixture of 4 with each of 1, 2, and 3.

Fig 1.

A. Mixtures of salts.

(1) M/20 Sodium cinnamate, M/20 sodium trichloracetate, M/2 sodium sulphate.

(2) M/20 Sodium cinnamate, M/20 potassium benzene sulphonate, M/2 sodium sulphate.

(3) M/20 Sodium cinnamate, M/20 sodium terephthalate, M/2 sodium sulphate.

In these cases the curve of the mixture is identical with that of M/20 sodium cinnamate alone, within the experimental error (Fig.1). The surface tension lowering produced by sodium cinnamate is in each case greater than that produced by the other component and it appears to be exclusively adsorbed.

(4) M/20 Sodium cinnamate, M/20 sodium phthalate, M/2 sodium sulphate.

(5) M/20 Sodium salicylate, M/20 sodium o-toluate, M/2 sodium sulphate.

(6) M/20 Potassium benzene sulphonate, M/20 sodium trichloracetate, M/2 sodium sulphate.

(7) M/20 Sodium terephthalate, M/20 sodium trichloracetate, M/2 sodium sulphate.

In these cases the constituent listed first causes by itself a greater surface tension lowering than the second. The adsorption curve of the mixture is only slightly higher than that of the first constituent, which is therefore almost exclusively adsorbed.

(8) M/20 p-Toluene sulphonic acid, M/20 tetra methyl ammonium hydroxide, M/2 sodium sulphate.

This /

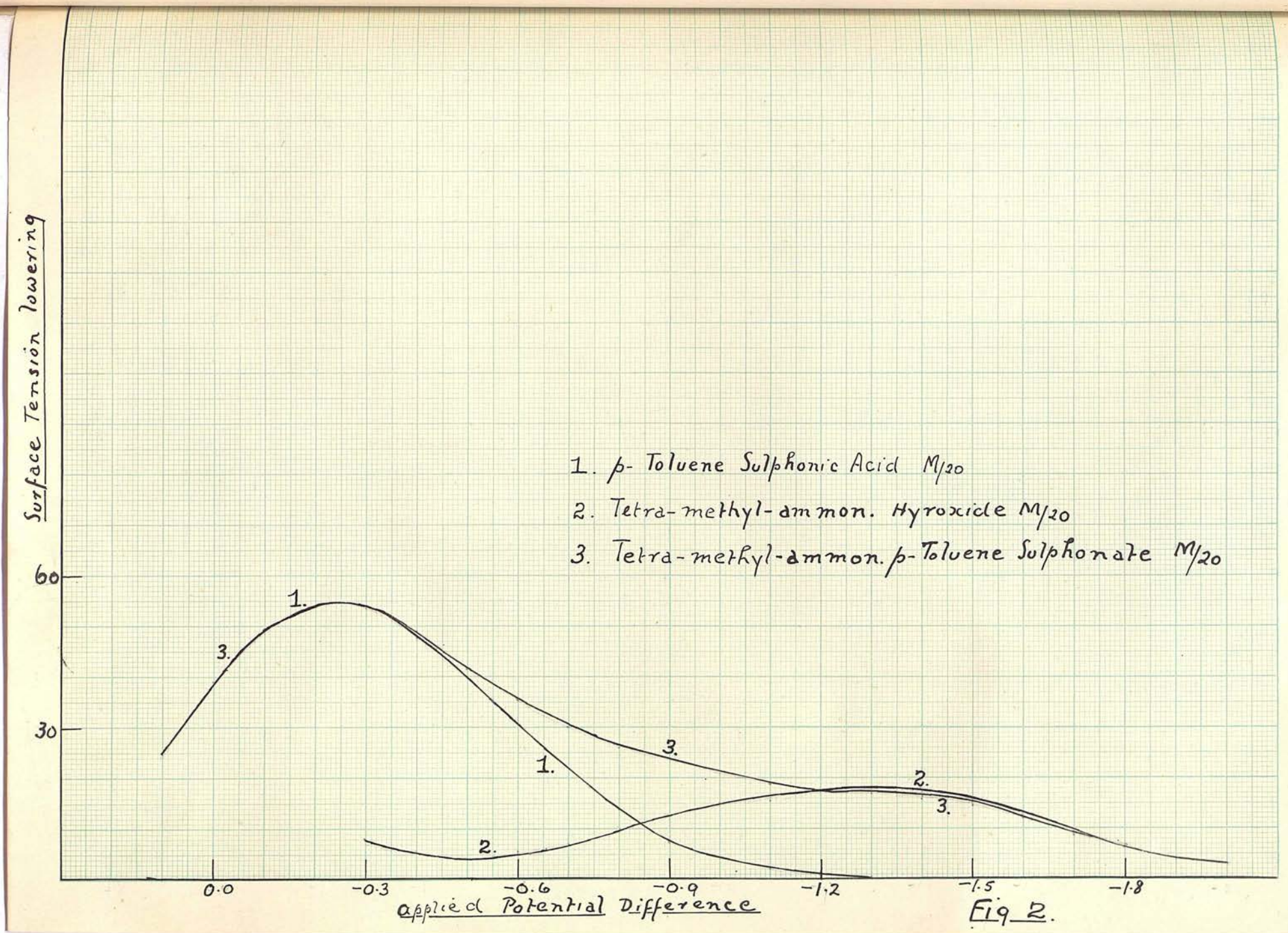
Surface Tension lowering
60
30
1. p- Toluene Sulphonic Acid M/20
2. Tetra-methyl-ammon. Hyroxide M/20
3. Tetra-methyl-ammon. p-Toluene Sulphonate M/20
1.
3.
1.
3.
2.
3.
2.
0.0
-0.3
-0.6
-0.9
-1.2
-1.5
-1.8
Applied Potential Difference

Fig 2.

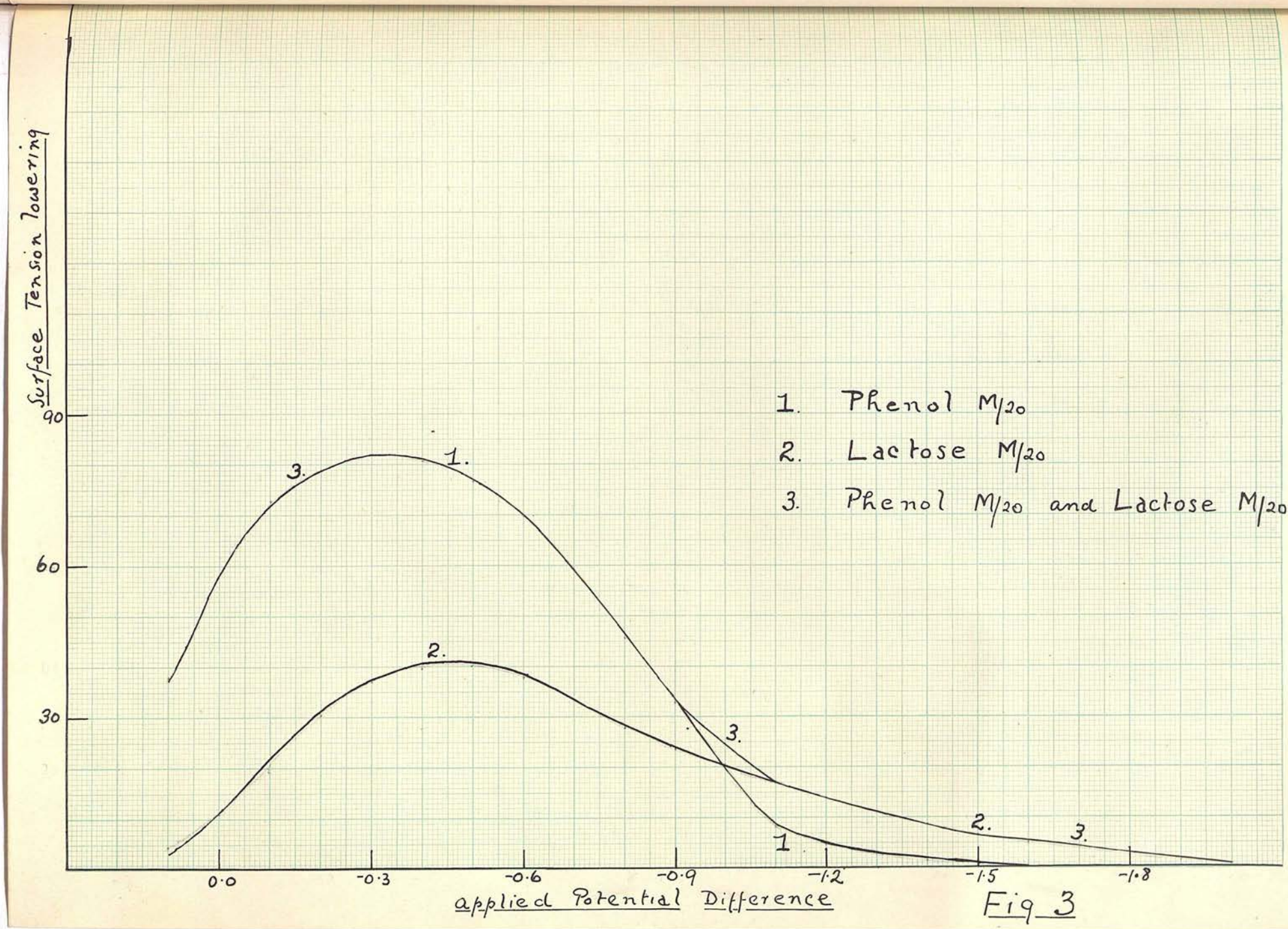
Surface Tension lowering
90
60
30
1. Phenol M/20
2. Lactose M/20
3. Phenol M/20 and Lactose M/20
0·0
-0·3
-0·6
-0·9
-1·2
-1·5
-1·8
applied Potential Difference

Fig 3

This solution, containing a salt of a strong organic acid with a strong organic base, is of interest because it contains both surface-active positive and negative ions. The adsorption curve is approximately the sum of the curves of the acid and base respectively showing that positive and negative ions whose maximum adsorptions occur at widely separated potential differences do not interfere with each other's behaviour. (Fig. 2)

B. Mixtures of non-ionised substances.

(9) M/20 phenol, M/20 lactose, M/2 sodium sulphate.

The adsorption curves of phenol and lactose cross at about -1.0 volt, the phenol curve being the higher to the left of the point of intersection, the lactose curve to the right. The curve of the mixture coincides with the phenol curve from +0.1 to -0.9 volts and with the lactose curve from -1.1 to -2.0 volts (Fig.3). The constituent which causes the greatest lowering of the surface tension is therefore exclusively adsorbed on each side. Between -0.9 and -1.1 volts, the mixture curve is higher than that of either constituent indicating the adsorption of both constituents.

(10) M/100 Caffein, M/20 lactose, M/2 sodium sulphate, Similar to (9).

(11) M/100 Caffein, M/20 phenol, M/2 sodium sulphate. This system is of interest because the maximum surface tension/

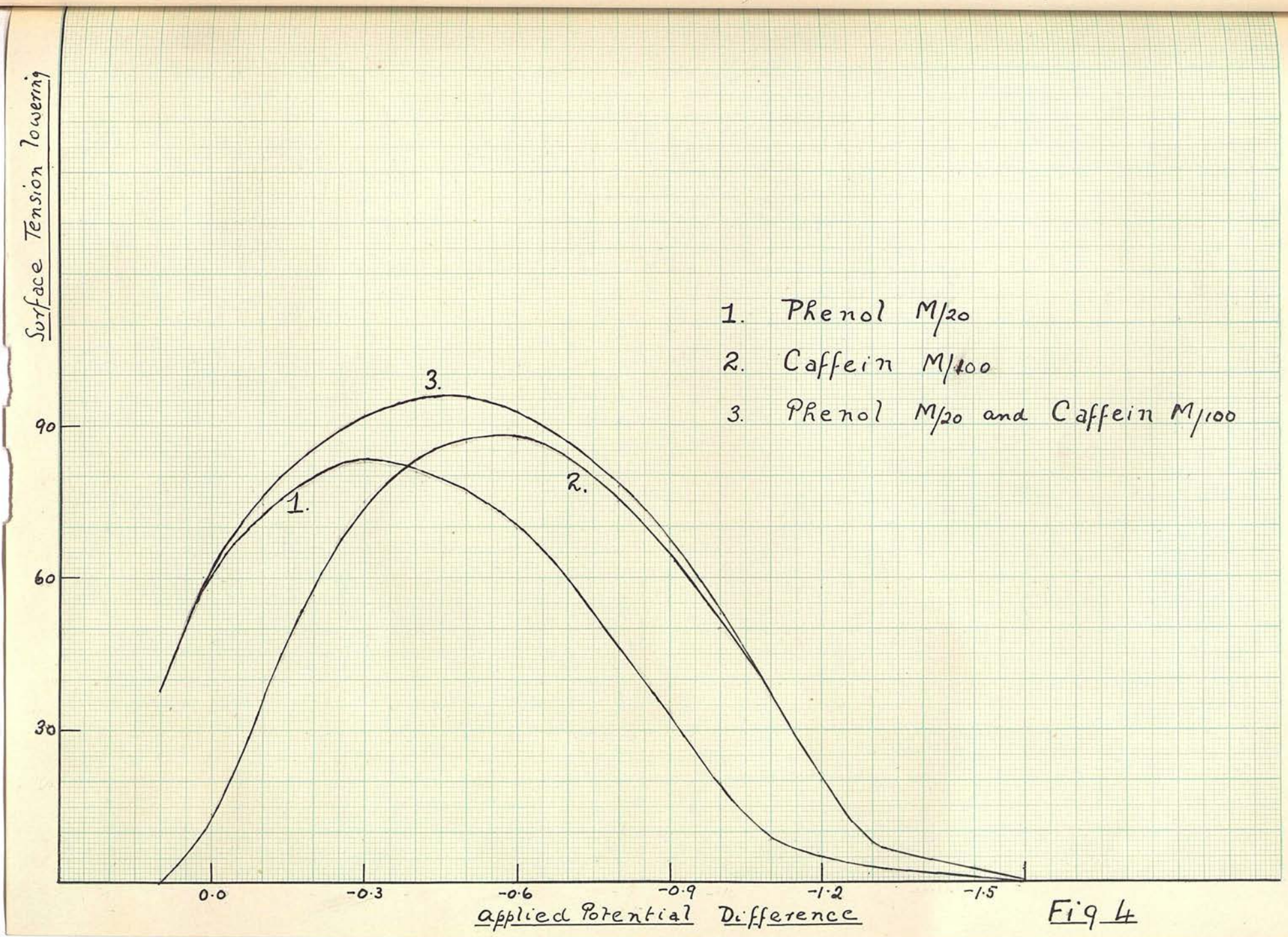
Surface Tension lowering
90
60
30
1.
2.
3.
1. Phenol M/20
2. Caffein M/100
3. Phenol M/20 and Caffein M/100
0·0
-0·3
-0·6
-0·9
-1·2
-1·5
applied Potential Difference

Fig 4

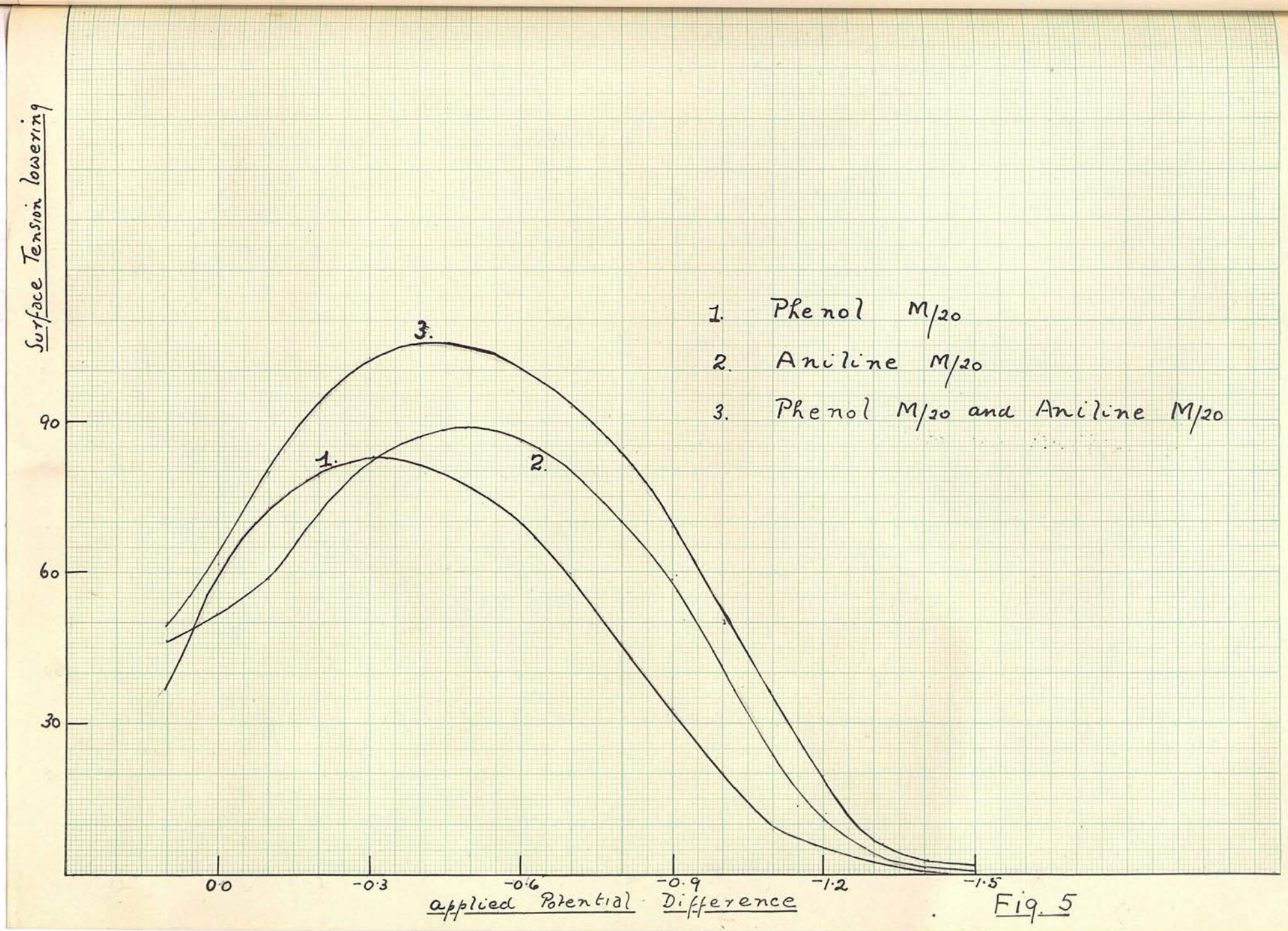
Surface Tension lowering
90
60
30
1.
2.
3.
1. Phenol M/20
2. Aniline M/20
3. Phenol M/20 and Aniline M/20
0·0
-0·3
-0·6
-0·9
-1·2
-1·5
applied Potential Difference

Fig. 5

tension lowerings of Caffein (M/100) and phenol (M/20) are nearly the same, but the potentials at which they occur differ by 0.25 volts. The adsorption curves cross at 0.4 volts (Fig.4). The curve for the mixture is higher than that of either constituent in the region of their point of intersection, but approaches the higher curve at each side.

(12) M/100 Caffein, p-toluidine (sat.)*, M/2 sodium sulphate.

In this system both components give adsorption curves with maxima of approximately the same height at nearly the same potentials (0.5 to 0.56 volts). The adsorption curve of the mixture is greater than that of either component, but is less than the sum of the single component curves. At the extreme left, where the difference between the lowerings of the single components is greatest, it is noteworthy that the mixture curve approaches the higher (p-toluidine) curve.

(13) M/20 Aniline, M/20 phenol, M/2 sodium sulphate.

Similar to (12) (Fig.5).

C. Mixtures of salts and non-ionised molecules.

(14) M/20 Phenol, M/10 sodium benzoate, M/2 sodium sulphate.

The/

* Curve for p-toluidine (sat.) in M/2 sodium sulphate for comparison is taken from Gouy (Ann. de Chim. et Phys. 1906, 91, 121).

The effect of the mixture is greater than that of either component separately, but much less than the sum of their separate effects. The curves for benzoic acid_sodium benzoate mixtures given in Part I are also significant in this connection.

Discussion.

It is evident that when two active substances of the same type (i.e. both ions or both non_ionised molecules) are present in solution, and one of them separately causes a considerably greater surface tension lowering than the other over the whole range of potential differences, the surface tension lowerings caused by the mixture are nearly identical with those of the first substance. It can easily be shown that, under these conditions, the second substance is not adsorbed from the mixture. According to the Gibbs equation, applied to a solution containing two solutes A and B, if we fix the interface so that the adsorption of the solvent is zero,

$$d\gamma = -\eta_s dt - \Gamma_A d\mu_A - \Gamma_B d\mu_B$$

where γ is the surface tension, η_s the superficial entropy, Γ_A, Γ_B the amounts of A and B adsorbed and μ_A and μ_B their chemical potentials (or partial free energies per unit mass). When the surface tension in solutions in which μ_A has a constant value is not affected by increasing the concentration of B.

$$\left(\frac{d\gamma}{d\mu_B}\right)_{t\ \mu_A V} = -\Gamma_B = 0$$

i.e. the adsorption of B is zero. In these cases we have therefore the exclusive adsorption of the more active constituent.

When the two substances separately cause nearly equal surface tension lowerings, the curve of the mixture is greater than either of the single curves, but much less than the sum of the two. In these cases selective action in the interface occurs, but it is not possible to determine by the present measurements, the relative amounts adsorbed of the two constituents. When the adsorption curves of the two substances cross each other, we have found several cases in which the curve of the mixture is close to the higher branch on each side of the point of intersection. Near the point of intersection the curve of the mixture is higher than that of either constituent, showing that both substances are present in the adsorbed layer. With mixtures of active neutral molecules and ions, it appears that the complete exclusion of the less active component (usually the ion) does not occur so readily.

In a recent paper, C. Wagner (Z. physikal. Chem., A, 1929, 143, 389) has given measurements of the surface tension at the air-solution interface of aniline-phenol mixtures in aqueous solution, and has found that in certain cases, the surface tension lowering of the mixture is greater than the sum of the separate lowerings of the constituents (cf.

mixture/

mixture (13)). He attributes this effect to the presence of one constituent increasing the adsorption of the other. In none of the mixtures investigated by us (with the exception of the solution containing active positive and negative ions, mixture (8)), is the total surface tension lowering as great as the sum of the two separate lowerings. It is possible that the amount of phenol adsorbed from the mixture at the air-solution interface is insufficient to cause the exclusion of aniline, and that owing to some interaction between aniline and phenol a greater amount may be adsorbed in the presence of each other.

Selective adsorption, the existence of which is clearly demonstrated by these results, must have important physiological implications since adsorptive processes play an important role in plant and animal organisms. Since it may also occur at solid-gas interface it may also have an important bearing on problems of heterogeneous catalysis.

Experimental.

The experimental details are the same as described in Part I. The measurements, which were carried out in an electrometer of the Smith-Gouy type, at room temperature, are given in Table I. Every curve was determined at least twice, and in a few cases in which the mixtures showed capillary viscosity ample time was allowed for the equilibrium value of each reading to be reached. Some of the comparison curves are given in Part I, the others are listed here.

TABLE I.

Electrocapillary curves of solutions of organic substances.

V	Sodium Sulphate M/2 (A)	Sodium Sulphate M/2 (B)	Sodium Sulphate M/2 (C)
+ 0.1	865.4	855.7	861.3
0.0	911.7	907.5	910.2
- 0.1	946.5	944.7	947.8
- 0.2	972.0	971.8	975.0
- 0.3	991.3	991.0	991.9
- 0.4	998.7	999.2	999.3
- 0.5	1000.4	1000.4	1000.6
- 0.6	997.4	996.8	997.0
- 0.7	987.7	987.0	986.3
- 0.8	972.2	971.7	972.1
- 0.9	953.1	951.7	953.0
- 1.0	930.7	928.6	928.3
- 1.1	901.7	901.4	900.0
- 1.2	872.1	870.3	870.0
- 1.3	837.2	835.5	834.8
- 1.4	798.6	796.8	794.8
- 1.5	756.1	753.4	753.0
- 1.6	708.5	706.6	704.9
- 1.7	657.9	656.5	653.7
- 1.8	603.4	600.6	597.0
- 1.9	542.8	540.4	536.8
- 2.0	477.2	474.9	470.2

V	Sodium Cinnamate M/20	Mixture Sodium Cinnamate M/20 and Sodium trichloracetate M/20	Mixture Sodium Cinnamate M/20 and Potassium Benzene Sulphonate M/20
+ 0.1	810.3	-	-
0.0	845.8	844.6	845.6
- 0.1	870.6	870.2	872.2
- 0.2	891.2	891.6	891.6
- 0.3	908.7	909.5	908.5
- 0.4	921.2	921.8	921.2
- 0.5	932.1	933.2	933.0
- 0.6	937.9	937.5	937.9
- 0.7	940.2	940.2	940.0
- 0.8	937.1	936.9	936.6
- 0.9	928.3	928.1	928.0
- 1.0	914.0	914.0	913.4
- 1.1	893.7	894.4	894.1
- 1.2	866.5	866.9	865.9
- 1.3	833.6	834.0	833.0
- 1.4	795.0	795.0	793.8
- 1.5	752.7	753.6	752.3
- 1.6	706.1	706.3	705.5
- 1.7	655.5	655.7	654.6
- 1.8	600.5	599.7	599.7
- 1.9	-	-	-
- 2.0	-	-	-
	B	B	B

V.	Sodium terephthalate M/20	Mixture Sodium cinnamate M/20 and Sodium terephthalate M/20	Mixture Sodium cinnamate M/20 and di-Sodium phthalate M/20	Sodium o-Toluate M/20
+ 0.1	-	-	808.1	841.0
0.0	858.5	843.0	845.8	876.4
- 0.1	891.7	870.5	870.2	904.2
- 0.2	919.0	890.8	891.3	925.7
- 0.3	941.3	908.5	909.1	942.7
- 0.4	960.6	920.1	919.2	957.7
- 0.5	971.7	932.6	927.5	966.2
- 0.6	978.1	937.9	933.7	970.0
- 0.7	977.1	940.6	935.0	968.1
- 0.8	968.2	937.2	935.3	958.5
- 0.9	950.6	927.0	928.1	944.7
- 1.0	928.0	913.4	914.2	923.7
- 1.1	900.3	893.5	892.8	897.3
- 1.2	870.2	865.7	866.6	868.5
- 1.3	835.6	829.7	833.7	834.9
- 1.4	797.2	793.0	794.7	796.0
- 1.5	754.6	751.4	752.2	751.9
- 1.6	707.9	705.1	706.7	705.2
- 1.7	656.5	654.2	655.3	654.7
- 1.8	601.5	598.5	599.7	598.7
- 1.9	-	-	-	-
- 2.0	-	-	-	-
	B	B	B	B

V	Mixture Sodium salicylate M/20 and Sodium o-toluate M/20	Mixture Potass. benzene sulphonate M/20 and Sodium Tri-Chloracetate M/20	Mixture Sodium terephthal-ate M/20 and Sodium trichlor-acetate M/20	Tetra-Methyl ammonium hydroxide M/20.
0.1	802.4	-	-	-
0.0	839.8	879.9	858.3	-
0.1	866.7	906.2	891.0	-
0.2	887.9	928.1	918.1	-
0.3	908.7	944.6	941.6	983.2
0.4	923.7	956.7	958.3	992.9
0.5	936.8	964.4	968.0	996.7
0.6	942.8	971.7	976.4	991.9
0.7	947.4	970.6	977.6	979.7
0.8	945.2	963.7	968.3	962.2
0.9	937.0	948.6	951.1	940.9
1.0	920.3	927.4	929.0	915.0
1.1	896.8	899.4	901.1	887.5
1.2	868.7	870.5	871.8	855.1
1.3	834.9	835.0	836.7	820.3
1.4	797.0	796.8	798.0	783.1
1.5	755.4	754.9	755.0	742.0
1.6	707.3	707.3	708.7	697.8
1.7	657.1	656.6	657.4	649.4
1.8	601.1	601.5	602.1	596.5
1.9	-	-	-	538.4
2.0	-	-	-	474.1
	B	B	B	A

V.	Mixture Tetra-methyl ammonium hydroxide M/20 and p-toluene sulphonic acid M/20	Phenol M/20	Lactose M/20	Mixture Phenol M/20 and Lactose M/20	Caffein M/100.
+ 0.1	-	828.2	859.8	829.1	864.4
0.0	-	850.4	900.7	848.8	898.7
- 0.1	898.0	875.0	929.3	874.2	911.0
- 0.2	919.5	894.6	941.0	894.8	916.3
- 0.3	937.8	910.5	954.5	910.3	918.4
- 0.4	950.6	919.8	960.4	920.0	918.3
- 0.5	960.2	925.3	962.0	926.1	915.7
- 0.6	962.8	929.3	960.2	927.3	911.8
- 0.7	977.9	929.5	954.5	928.9	906.0
- 0.8	946.8	927.3	945.3	927.0	898.7
- 0.9	929.4	920.7	930.0	920.0	889.8
- 1.0	909.5	911.3	910.0	906.6	881.5
- 1.1	883.9	894.0	885.2	885.0	866.1
- 1.2	855.3	866.6	857.8	858.5	852.4
- 1.3	822.3	833.7	826.1	826.3	829.1
- 1.4	785.1	796.7	790.2	790.7	792.7
- 1.5	743.4	754.8	750.1	750.3	752.3
- 1.6	699.2	708.7	704.0	704.3	707.7
- 1.7	650.0	657.8	653.8	653.3	656.7
- 1.8	596.6	602.9	600.2	600.9	601.7
- 1.9	538.0	542.0	541.1	541.6	541.8
- 2.0	-	477.1	476.5	477.1	476.4
	A	A	A	A	A

V.	Mixture Caffein M/100 and Lactose M/20	Mixture Caffein M/100 and Phenol M/20	Mixture Caffein M/100 and p-toluidine (satd).	Aniline M/20
+ 0.1	-	827.2	-	814.5
0.0	896.9	846.6	852.3	858.4
- 0.1	908.7	874.2	876.9	889.0
- 0.2	915.3	891.1	887.1	902.8
- 0.3	917.1	900.6	901.2	909.4
- 0.4	918.1	905.4	892.8	913.2
- 0.5	915.6	906.7	892.8	912.4
- 0.6	911.4	906.3	890.9	911.2
- 0.7	906.7	902.9	886.9	906.3
- 0.8	899.1	897.0	882.8	902.3
- 0.9	890.0	887.2	875.8	894.2
- 1.0	881.0	879.7	865.3	887.0
- 1.1	868.3	865.6	856.4	875.9
- 1.2	852.4	852.8	843.4	859.0
- 1.3	823.0	826.3	827.2	831.0
- 1.4	787.6	792.2	793.2	794.2
- 1.5	750.6	751.7	752.0	752.2
- 1.6	704.1	706.6	707.0	704.8
- 1.7	654.0	655.1	656.1	675.1
- 1.8	600.6	600.6	600.8	597.5
- 1.9	541.1	540.2	540.8	536.8
- 2.0	476.5	475.2	476.4	470.2
	A	A	A	C

V.	Mixture Aniline M/20 and Phenol M/20	Mixture Phenol M/20 and Sodium benzoate M/20
+ 0.1	810.4	800.1
0.0	846.0	837.9
- 0.1	866.8	864.0
- 0.2	881.6	883.5
- 0.3	889.2	898.5
- 0.4	894.6	908.7
- 0.5	896.5	914.9
- 0.6	896.3	918.6
- 0.7	893.6	920.5
- 0.8	889.8	917.8
- 0.9	883.7	913.8
- 1.0	876.0	908.5
- 1.1	864.3	892.8
- 1.2	850.4	866.6
- 1.3	828.0	833.3
- 1.4	792.8	795.9
- 1.5	751.0	753.4
- 1.6	704.0	707.8
- 1.7	653.6	655.8
- 1.8	597.0	600.2
- 1.9	536.9	539.6
- 2.0	470.3	473.7
	C	A

SUMMARY.

1. The electrocapillary curves of a number of solutions containing two active substances have been determined.

2. It is shown that in mixtures of substances of the same type (ions or non-ionised molecules), if one compound causes a greater surface tension lowering than the other over the whole range of potential differences, it alone is adsorbed.

3. When the components cause nearly the same surface tension lowerings, both substances are adsorbed from the mixture.

4. When the adsorption curves cut each other, several cases have been found at which one component is exclusively adsorbed at potential differences below the point of intersection and the other at p.ds. above the point of intersection.

5. Except in the case of a solution containing active positive and negative ions, the surface tension lowerings produced by the mixtures are less than the sum of those produced by the components separately.

P A R T III.

ADSORPTION EFFECTS IN MIXTURES OF TWO ACTIVE COMPONENTS. THE EFFECT OF VARYING THE CONCENTRATION OF THE COMPONENTS.

It has been shown in Part II, that in aqueous solutions containing two capillary active solutes, if one solute causes a much greater surface tension lowering than the other (where both solutes are similar - both ionisable or both non-ionisable substances), then the more active component is selectively adsorbed throughout the whole range of applied potential differences. When the adsorption curves of the individual solutes intersect, it has been shown that at some potentials complete selective adsorption of the more active constituent may be obtained and in the region of intersection partial selective adsorption of both components occurs.

The purpose of this investigation is to determine how selective adsorption is affected by varying the concentrations of the active solutes, and to consider how an approximate quantitative treatment may apply to the experimental data.

Since an intensive study requires a very large number of measurements, only a few typical cases can be investigated. For this purpose one example of each of the two following systems was investigated.

A. Mixtures of two capillary active solutes (ion-mixtures), showing complete selective adsorption over the whole range of applied potential differences.

and/

and B. Mixtures of two capillary active non-ionising solutes, the individual adsorption curves of which intersect.

A new interesting example of selective adsorption in a mixture of salicin and saccharose has also been obtained.

As in Parts I and II all the solutions are made up so as to be half-molar with respect to sodium sulphate.

A. Mixtures of Two Capillary Active Salts.

It was desirable to investigate selective adsorption with changing concentration employing two salts, the maxima of whose adsorption curves occur at approximately the same applied potential difference. For this purpose a new system was decided upon. The salts chosen were sodium cinnamate and sodium o-toluate, the maxima of whose adsorption curves occur at ca.-0.3 volts. The salts were prepared in the manner described in Part I.

The adsorption curves of the individual components determined were:-

	Sodium Cinnamate.		Sodium o-toluate.
(I)	M/20	(VIII)	M/20
(II)	M/40		
(III)	M/50		
(IV)	M/60		
(V)	M/100		
(VI)	M/150		
(VII)	M/300		

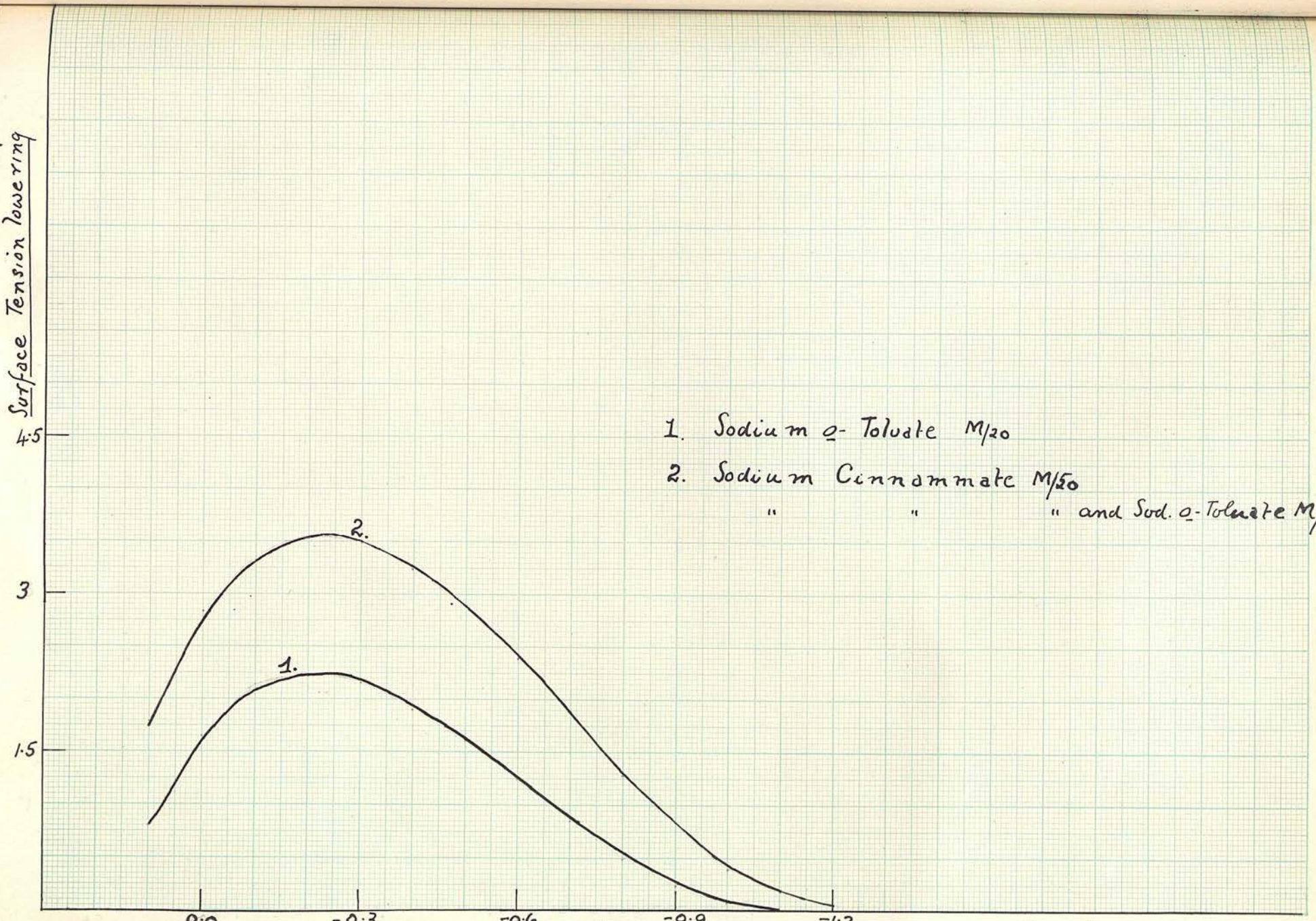
Surface Tension lowering
4·5
3
1·5
2.
1.
0·0
-0·3
-0·6
-0·9
-1·2
Applied Potential Difference
1. Sodium o- Toluate M/20
2. Sodium Cinnammate M/50
" " " and Sod. o- Toluate M/20

Fig 1.

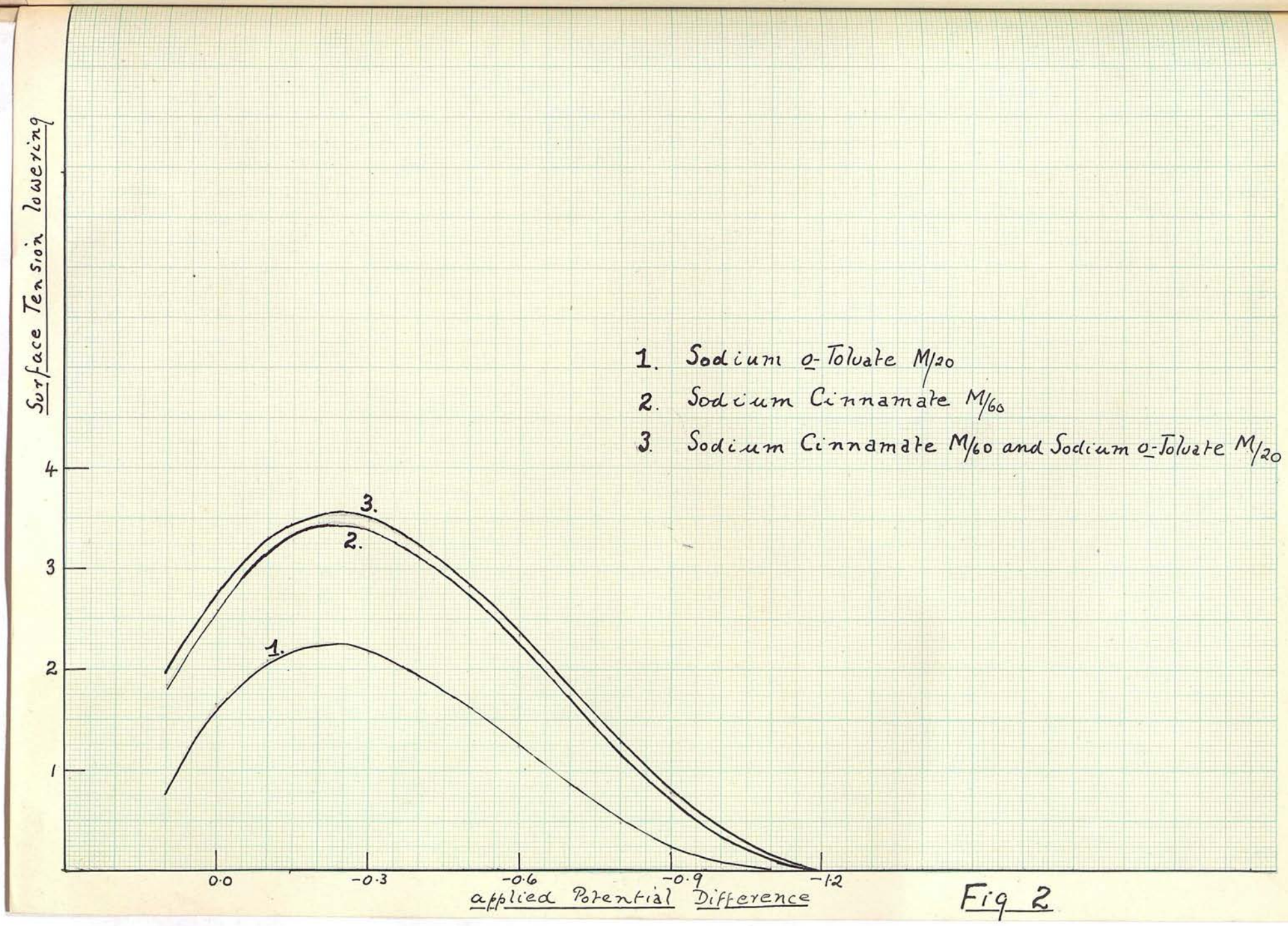
Surface Tension lowering
4
3
2
1
1. Sodium o-Toluate M/20
2. Sodium Cinnamate M/60
3. Sodium Cinnamate M/60 and Sodium o-Toluate M/20
3.
2.
1.
0·0
-0·3
-0·6
-0·9
-1·2
applied Potential Difference

Fig 2

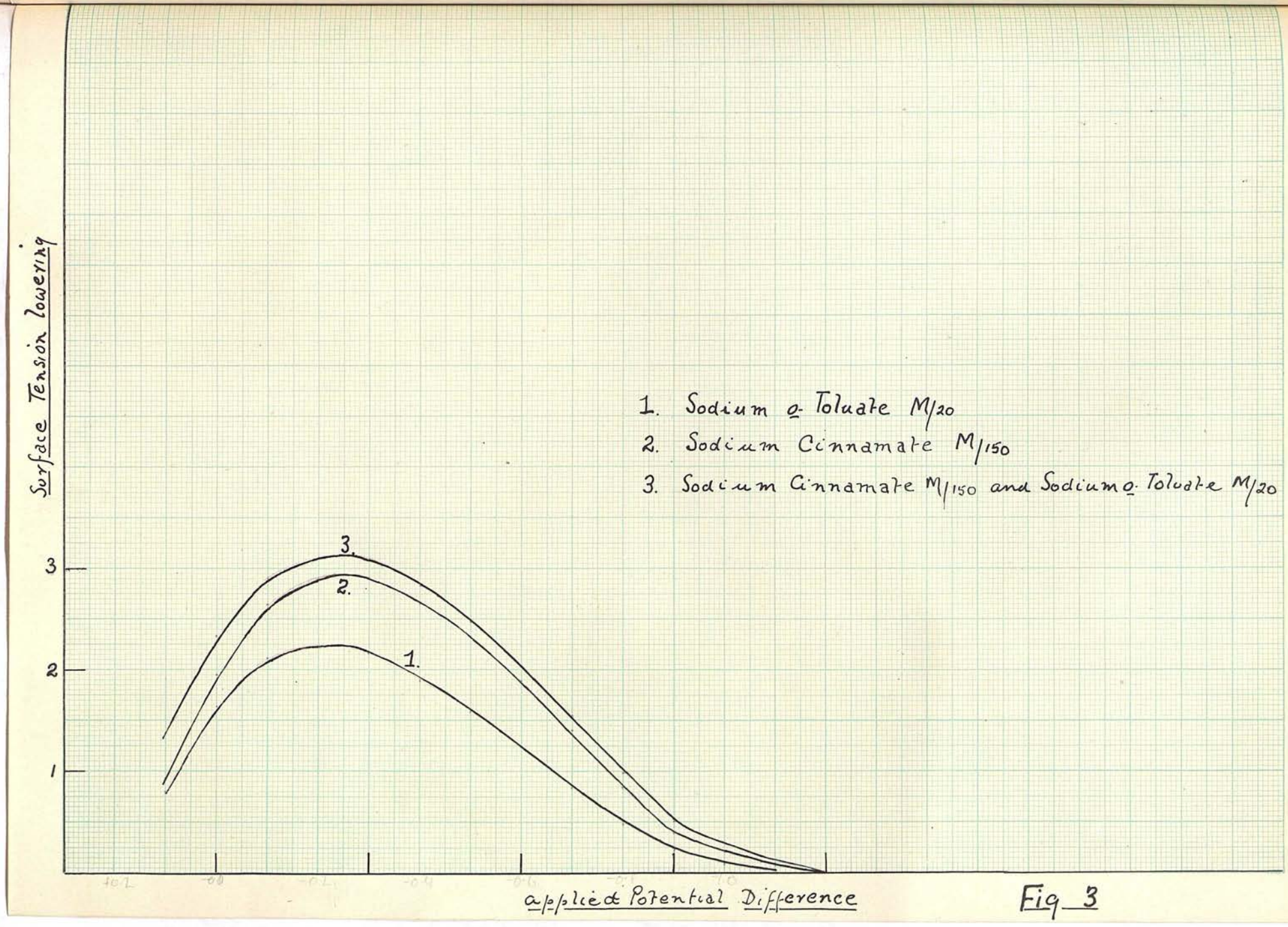
Surface Tension lowering
3
2
1
1. Sodium o- Toluate M/20
2. Sodium Cinnamate M/150
3. Sodium Cinnamate M/150 and Sodium o- Toluate M/20
3.
2.
1.
applied Potential Difference

Fig 3

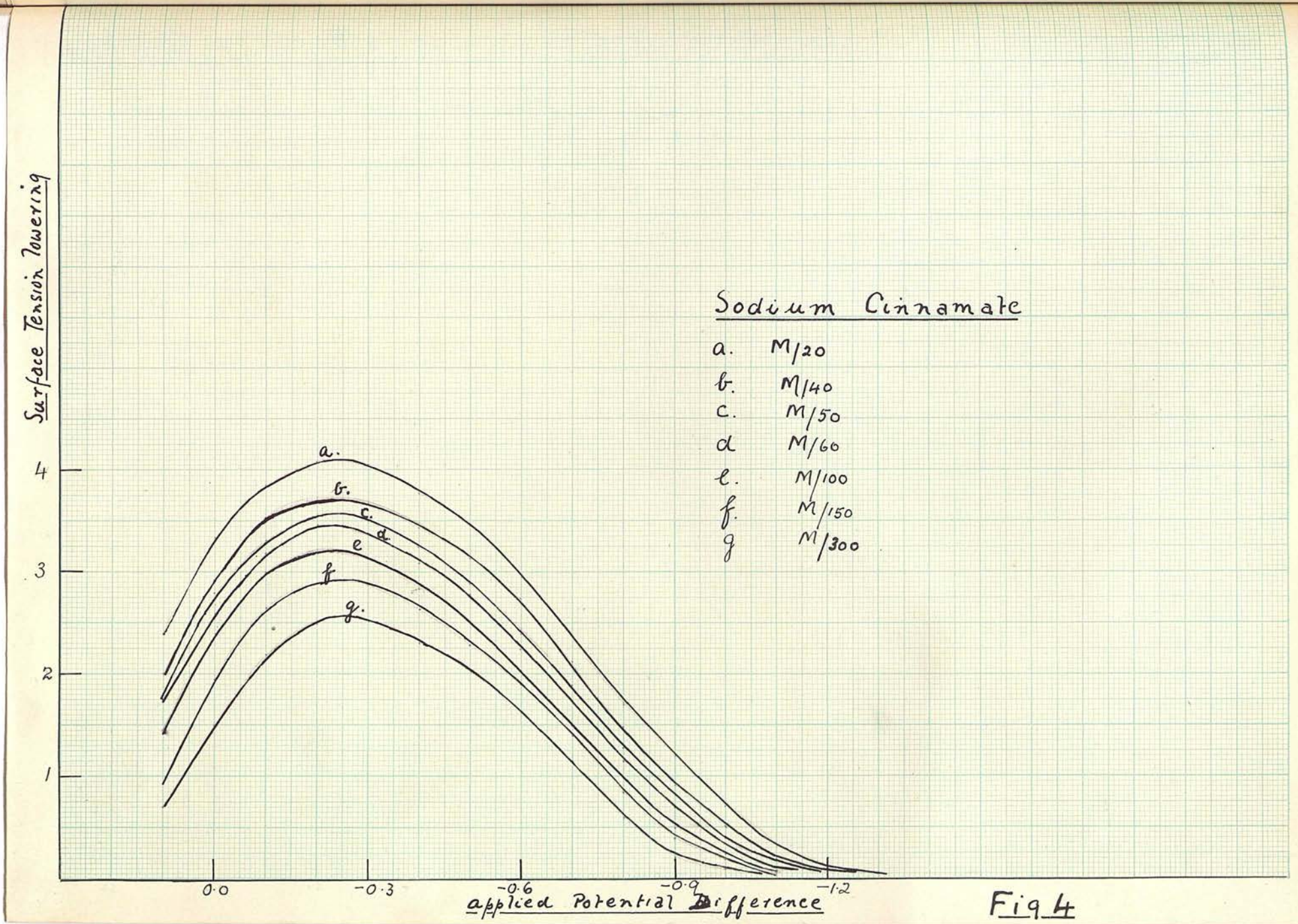
Surface Tension lowering
4
3
2
1
a.
b.
c.
d.
e
f
g.
0·0
-0·3
-0·6
-0·9
-1·2
applied Potential Difference
Sodium Cinnamate
a. M/20
b. M/40
c. M/50
d M/60
e. M/100
f. M/150
g M/300

Fig 4

The adsorption curves of the following mixtures were next determined:-

(1)	Sodium Cinnamate		M/20	and	Sodium	o-toluate		M/20
(2)	"	"	M/40	"	"	"	"	"
(3)	"	"	M/50	"	"	"	"	"
(4)	"	"	M/60	"	"	"	"	"
(5)	"	"	M/100	"	"	"	"	"
(6)	"	"	M/150	"	"	"	"	"

In mixtures (1), (2) and (3) the presence of the sodium o-toluate exerts no appreciable effect (Fig.1). In mixture (4) the presence of sodium o-toluate in the adsorption layer first becomes apparent (Fig.2). The presence of sodium o-toluate in the adsorption layer becomes still more appreciable in mixtures (5) and (6), but even in mixture (6) the lowering caused by sodium o-toluate is still comparatively small (Fig.3).

The difference in the surface tension lowerings between M/50 (Fig.4,C) and M/60 (Fig.4,D.) sodium cinnamate is quite small. An increase in ratio of $\frac{60}{50} = 1.2$ of sodium cinnamate or some smaller increase determines whether or not the adsorption of sodium o-toluate becomes measurable. The height at -0.3 volts (i.e. near the maxima) of the curves for M/50 and M/60 sodium cinnamate respectively are 70 and 67.5 scale units, so that the percentage difference in the surface tension lowerings is $\frac{70-67.5}{70} .100 =$ 3.5 per cent.

The interfacial tensions of M/50 sodium cinnamate and M/20 sodium o-toluate are 47.88 and 49.21 cms. of mercury/

mercury respectively at -0.3 volts (Table II), so that the percentage difference in the interfacial tensions with respect to M/50 Sodium cinnamate is $\frac{49.21 - 47.88}{49.21} .100 = 2.7$ per cent., i.e. a difference of 2.7% (or less) in interfacial tension is sufficient to prevent appreciable adsorption of the sodium o-toluate.

The measurements of the electrocapillary curves are given in Table II. The measurements are the interfacial tensions in centimetres of Mercury and no conversion is made to the Gouy standard.

B. Mixtures of Two Capillary Active Non-ionising Solutes.

The adsorption curve of the Phenol-Caffein mixture obtained in Part II shows points of special interest and indicated the possibility, by investigating mixtures over a range of concentrations, of calculating on the basis of Adsorption theory the approximate amounts of the two components which go to make up the adsorption curve of the mixture.

The adsorption curves of the separate components determined were:-

	Phenol.		Caffein
(I)	M/10	(VI)	M/50
(II)	M/20	(VII)	M/100
(III)	M/50	(VIII)	M/300
(IV)	M/100		
(V)	M/200		

The/

The adsorption curves of the following mixtures were next determined:-

(a)	(1)	Phenol	M/10	and	Caffein	M/100
	(2)	"	M/20	"	"	"
	(3)	"	M/50	"	"	"
	(4)	"	M/100	"	"	"
	(5)	"	M/200	"	"	"
and (b)	(1)	Caffein	M/50	and	Phenol	M/20
	(2)	"	M/100	"	"	"
	(3)	"	M/300	"	"	"

The measurements of the electrocapillary curves are given in Table III.

M/20 Salicin - M/2 Saccharose Mixture.

The adsorption curve of this mixture is of interest, since in this case, while the adsorption of the saccharose is not apparent in the higher parts of the curve - the mixture curve being coincident with that of the salicin alone - an appreciable effect due to the adsorption of saccharose is obtained at both the extreme ends (Fig.11). Since the solutions of these substances undergo changes on standing they are not suitable for prolonged investigation at various concentrations.

The measurements of the electrocapillary curves are given in Table IV.

DISCUSSION.

A. Sodium Cinnamate - Sodium o-Toluate Mixtures.

The apparent existence of complete selective adsorption of the sodium cinnamate in mixtures (1) (2) and (3), raises points of considerable interest. If it be supposed that the adsorption layer is of definitely fixed dimensions and capable of accommodating only a fixed number of molecules of a given type, then it is possible to understand why at a definite concentration of sodium cinnamate, M/20 say, the adsorption layer may be practically completely occupied with sodium cinnamate, so that an appreciable amount of sodium o-toluate molecules will be unable to enter the adsorption layer without squeezing out the more surface active sodium cinnamate molecules, (actually of course it is the ions which are concerned) and thus leading to an increase in the surface energy. If this premise is accepted, it would be expected that on reducing the amount of sodium cinnimate in the mixtures - the absolute amount of sodium cinnamate adsorbed therefore falling off - that space would be available for the less active sodium-o-toluate, the latter would then become adsorbed and the surface tension lowering of the mixture would thus be greater than that caused by the sodium cinnamate alone. Actually it is found however/

however, that even on reducing the sodium cinnamate concentration from M/20 to M/50 (mixture 3) - a corresponding decrease in the surface tension lowering ensueing - no measurable effect due to the presence of the toluate is observed. Even at the low concentration of M/150 sodium cinnamate in the mixture the addition of M/20 sodium o-toluate causes only a relatively small increase in the surface tension lowering (Fig.3).

One other point deserves notice. In mixture (4), where the effect of the sodium o-toluate first appears, the increase in the surface tension lowering becomes apparent throughout the whole range of applied potentials (Fig.2) and not merely at the points where the differences between the separate lowerings of both constituents is greatest, as might have been expected. If the surface tension lowerings are a measure of the variation of the amount adsorbed with the change in the electric field, then at high negative potentials from say -0.7 to -1.1 volts, where the adsorption curves fall off rapidly, it might be expected that the effect of the sodium o-toluate would tend to become negligable, this does not however appear to be the case. It is difficult to estimate what this means since so many factors are involved, but it clearly has a very significant bearing on the structure of surface layers.

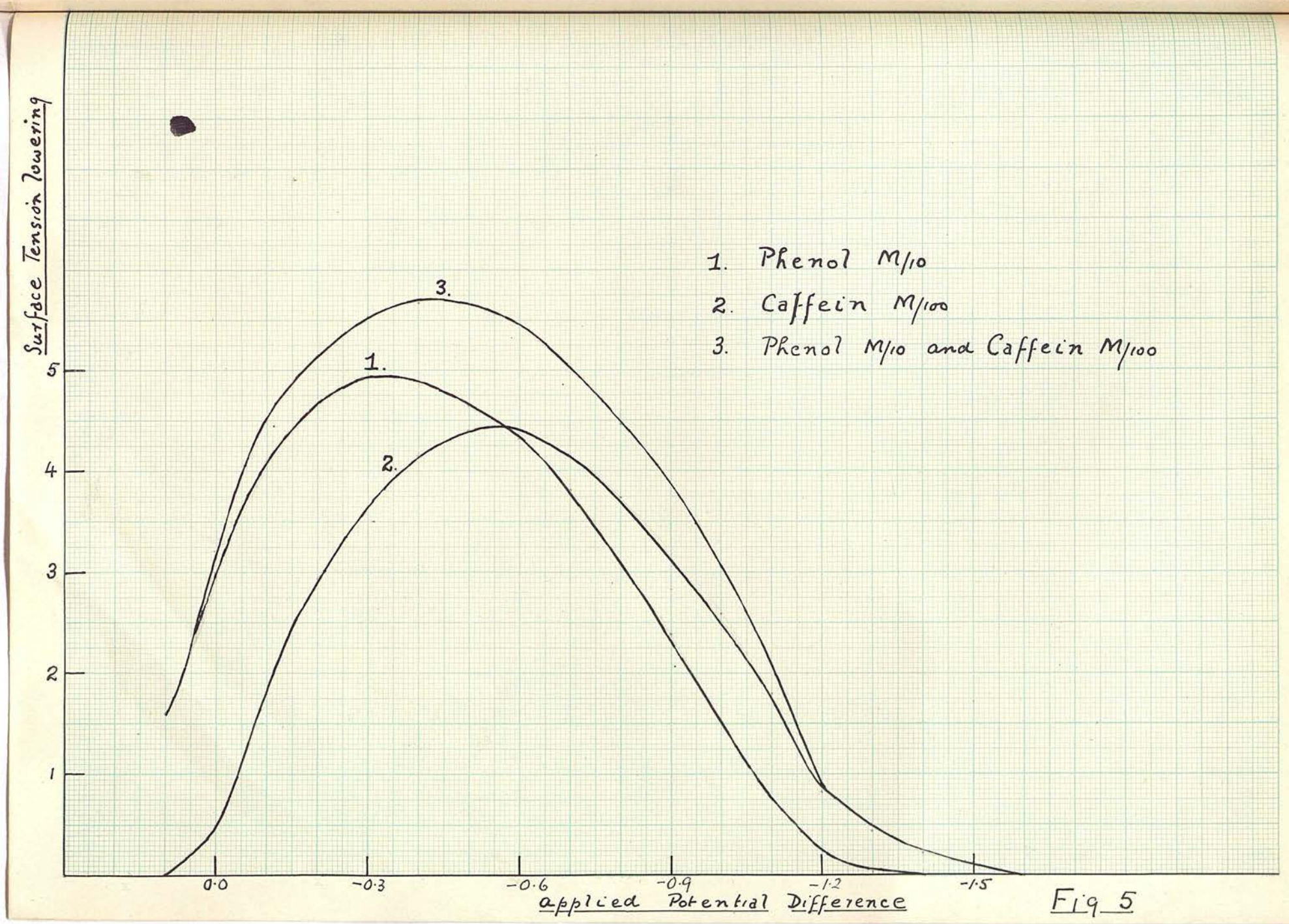
Surface Tension lowering
5
4
3
2
1
1.
2.
3.
1. Phenol M/10
2. Caffein M/100
3. Phenol M/10 and Caffein M/100
0·0
-0·3
-0·6
-0·9
-1·2
-1·5
applied Potential Difference

Fig 5

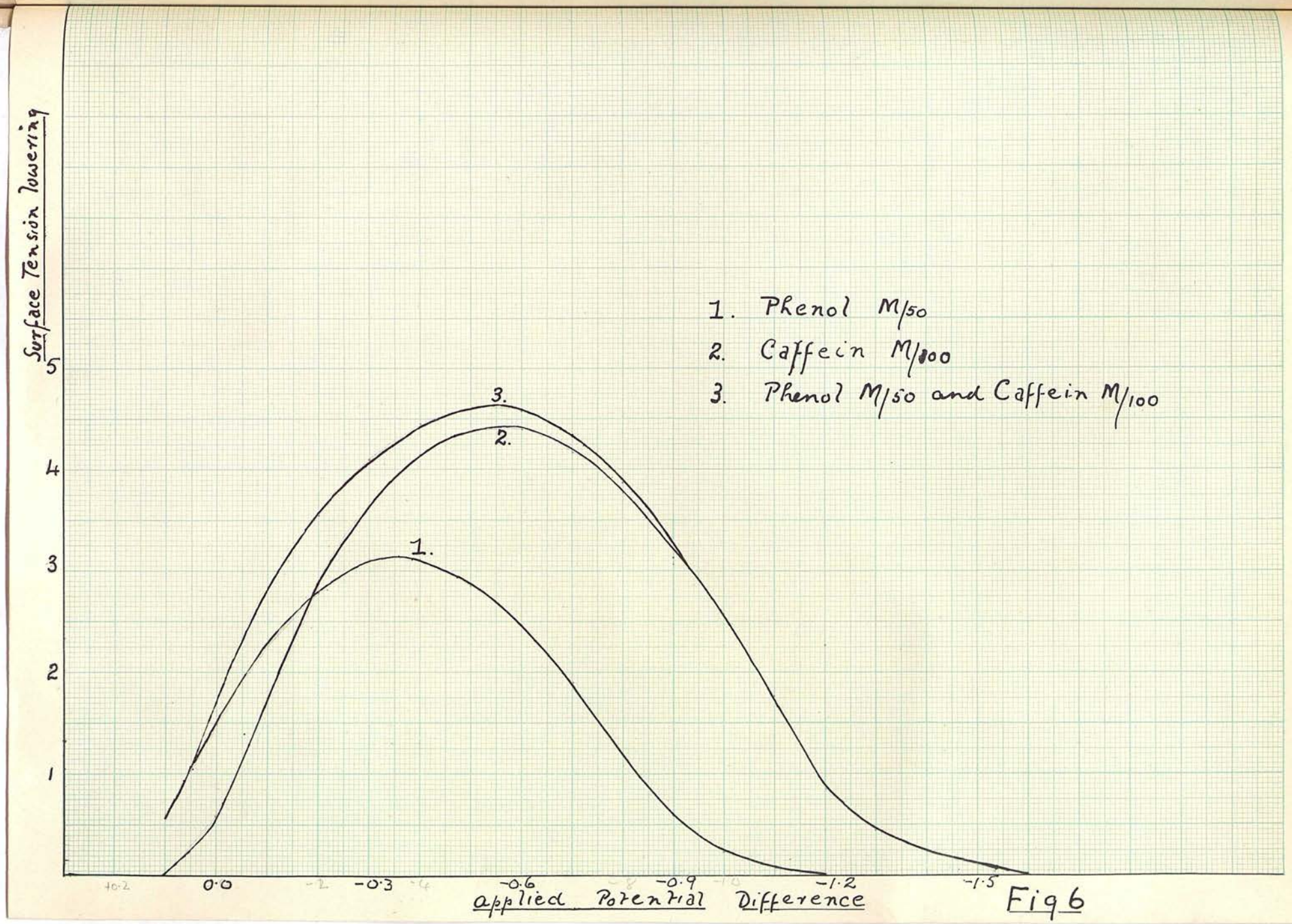
Surface Tension lowering
5
4
3
2
1
1. Phenol M/50
2. Caffein M/100
3. Phenol M/50 and Caffein M/100
3.
2.
1.
0·0
-0·3
-0·6
-0·9
-1·2
-1·5
applied Potential Difference

Fig 6

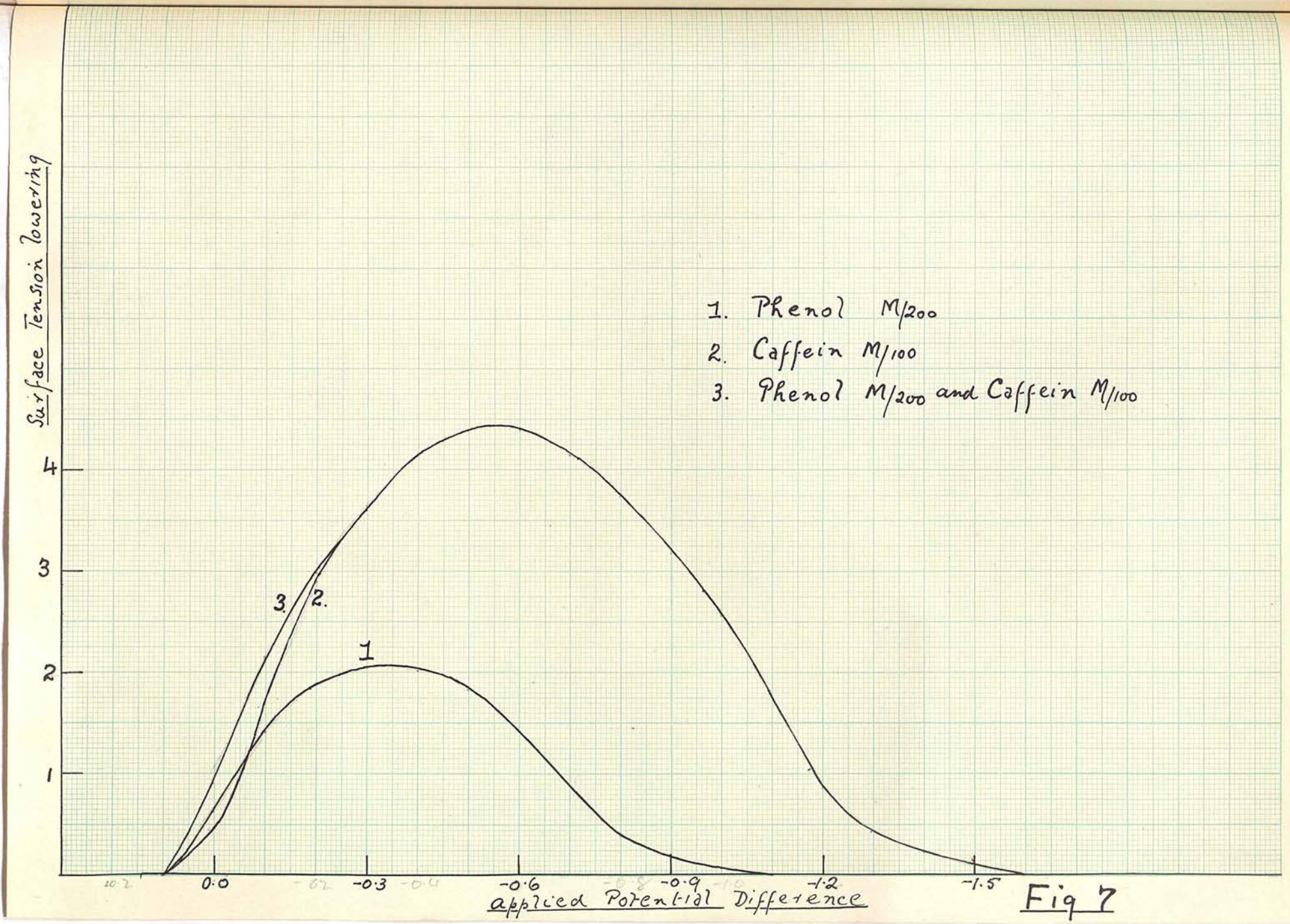
Surface Tension lowering
4
3
2
1
1. Phenol M/200
2. Caffein M/100
3. Phenol M/200 and Caffein M/100
3
2
1
10·2
0·0
-0·3
-0·6
-0·9
-1·2
-1·5
applied Potential Difference

Fig 7

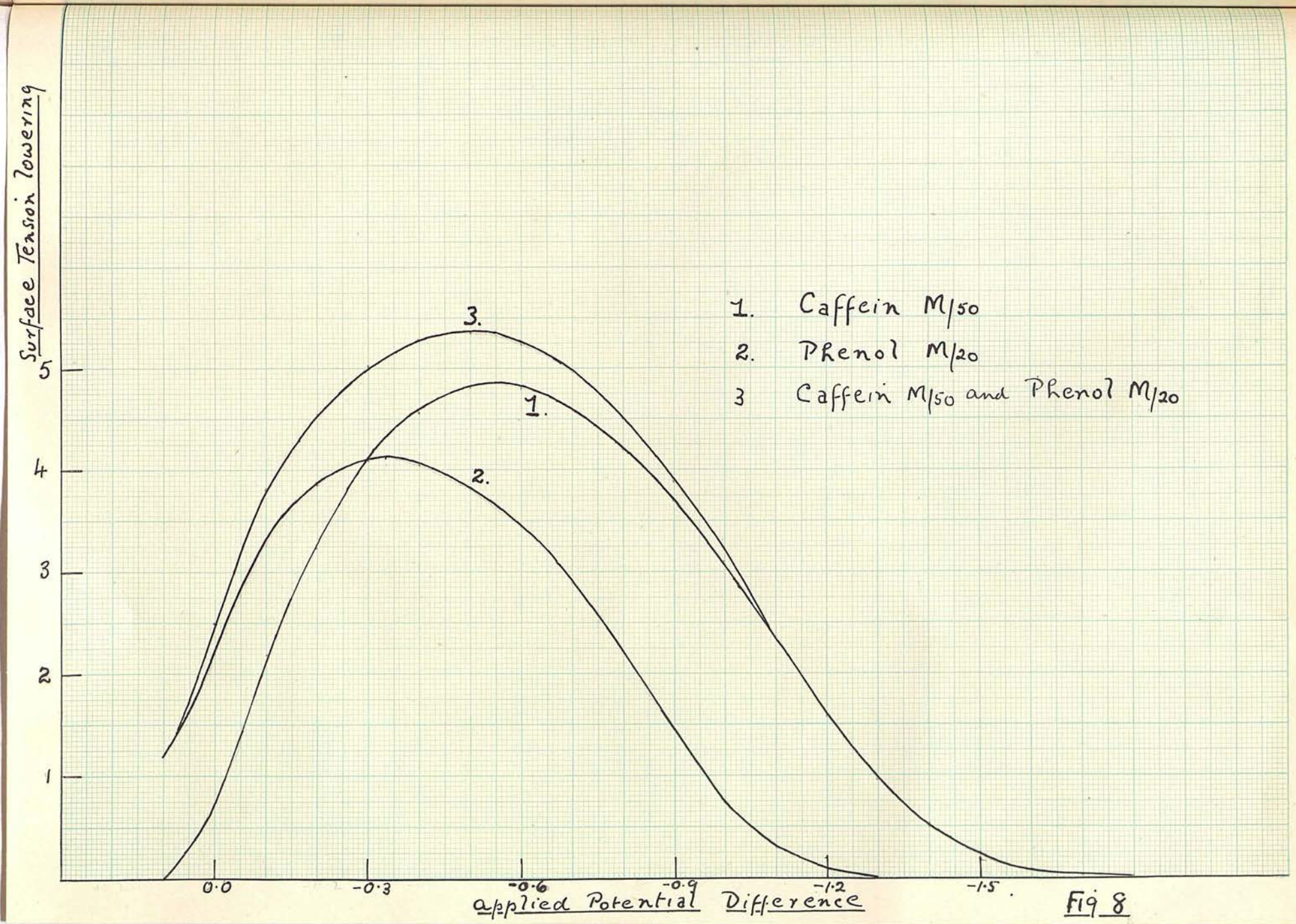
Surface Tension lowering
5
4
3
2
1
3.
1.
2.
1. Caffein M/50
2. Phenol M/20
3 Caffein M/50 and Phenol M/20
0·0
-0·3
-0·6
-0·9
-1·2
-1·5
Applied Potential Difference

Fig 8

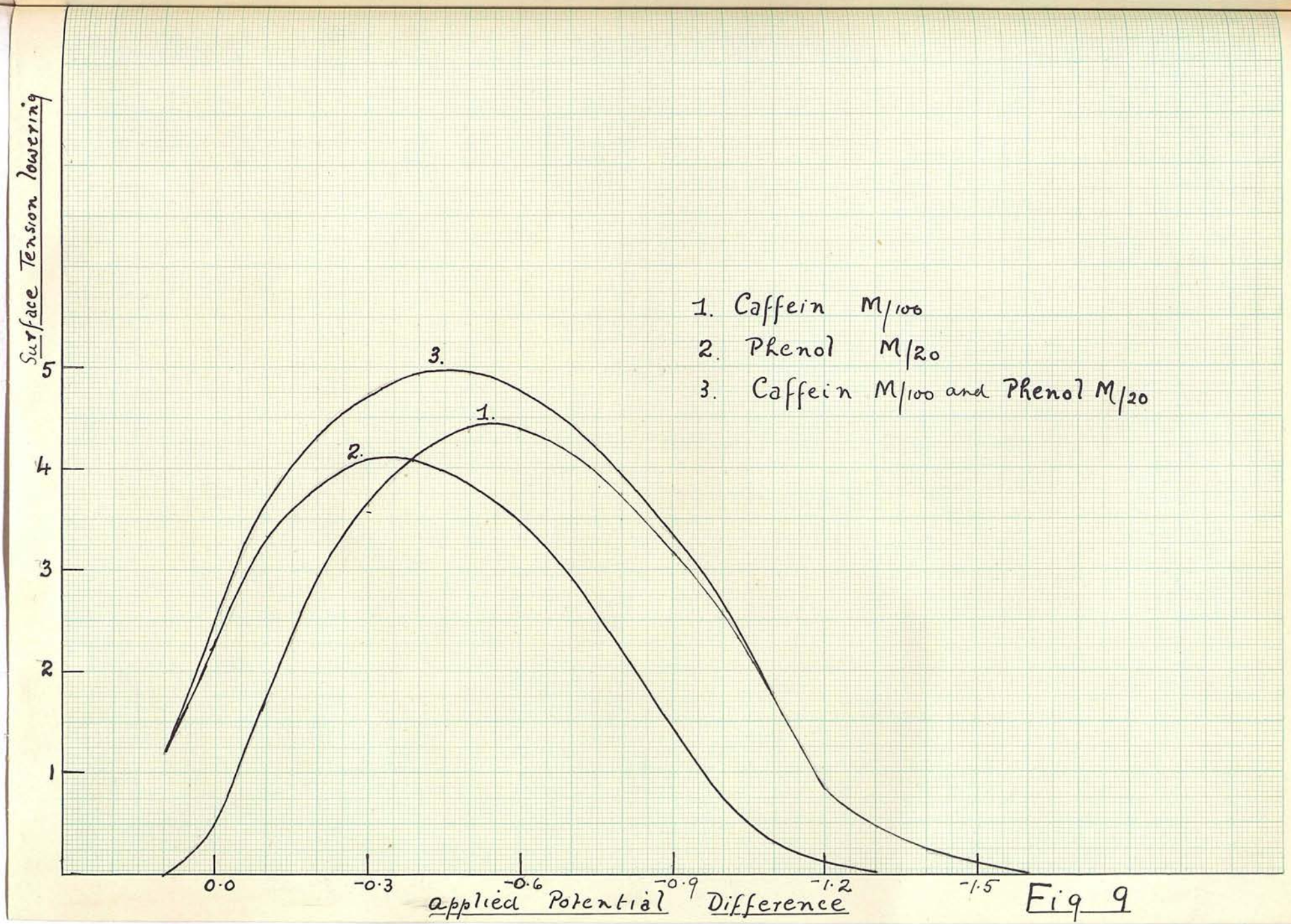
Surface Tension lowering
5
4
3
2
1
1. Caffein M/100
2. Phenol M/20
3. Caffein M/100 and Phenol M/20
3.
1.
2.
0·0
-0·3
-0·6
-0·9
-1·2
-1·5
applied Potential Difference

Fig 9

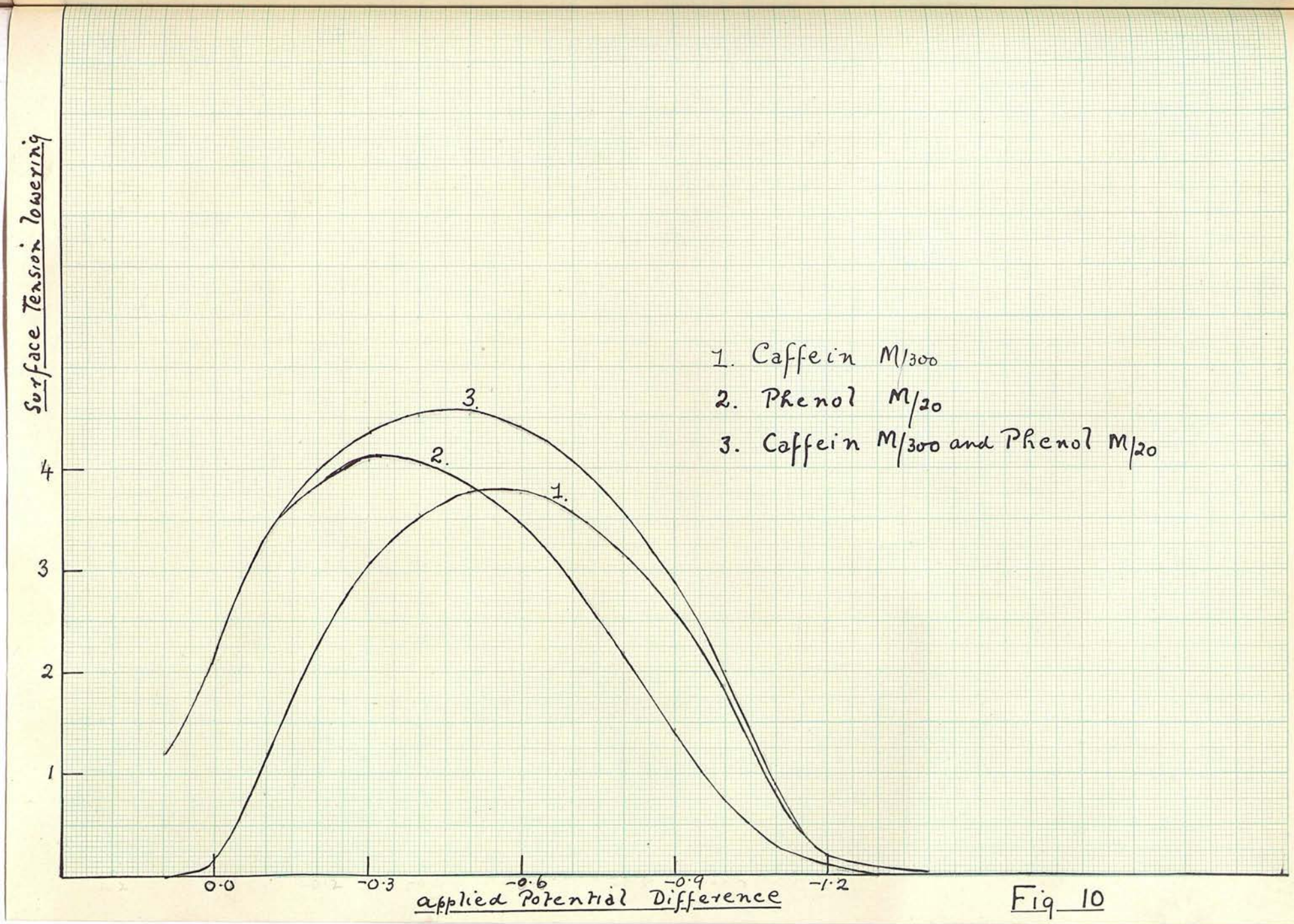
Surface Tension lowering
4
3
2
1
3.
2.
1.
0·0
-0·3
-0·6
-0·9
-1·2
applied Potential Difference
1. Caffein M/300
2. Phenol M/20
3. Caffein M/300 and Phenol M/20

Fig 10

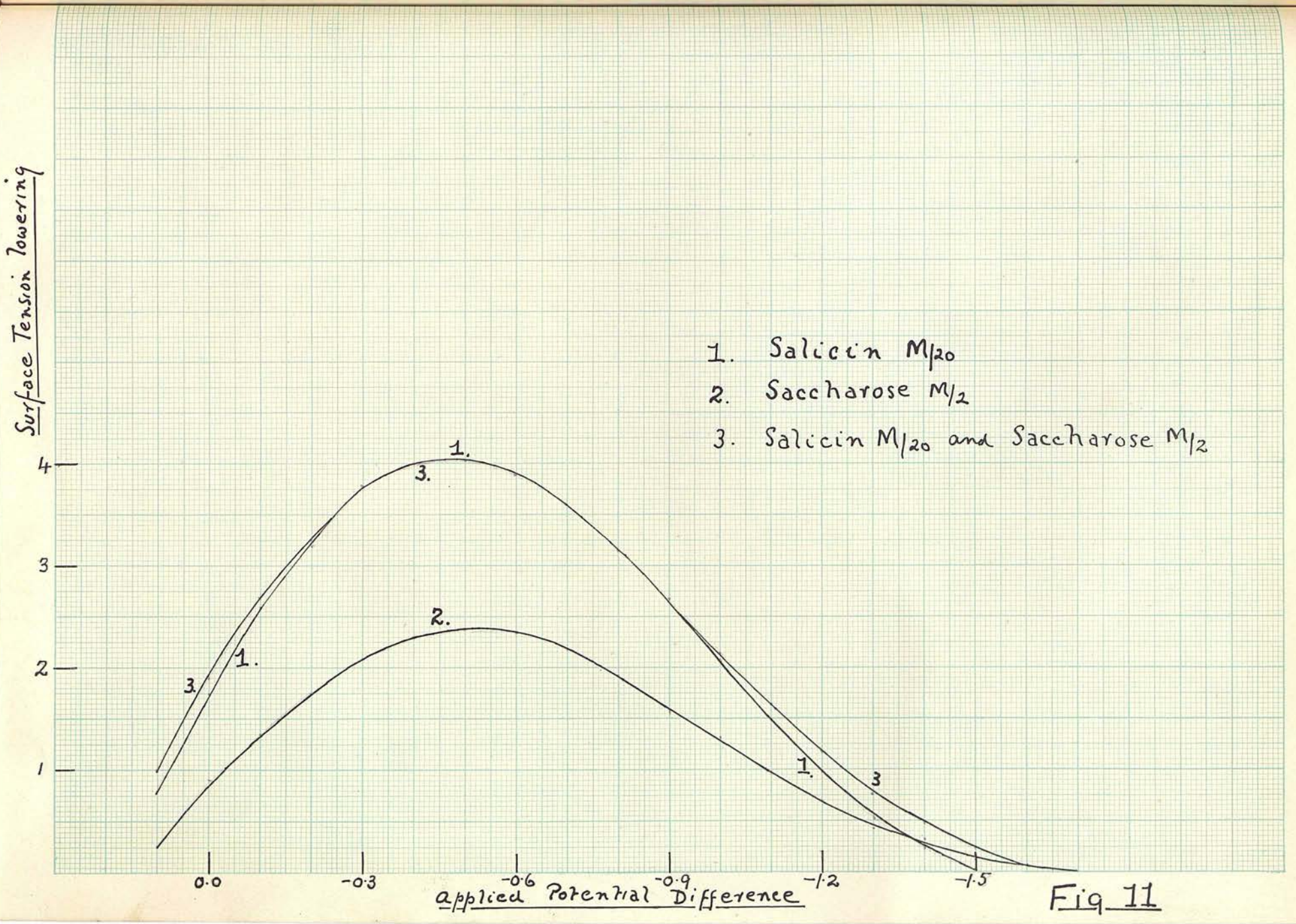
Surface Tension lowering
4
3
2
1
1. Salicin M/20
2. Saccharose M/2
3. Salicin M/20 and Saccharose M/2
1.
3.
2.
1.
3.
1.
3
0·0
-0·3
-0·6
-0·9
-1·2
-1·5
applied Potential Difference

Fig 11

B. Phenol-Caffein Mixtures.

The (a) curves (Figs. 5, 6, and 7) show clearly, that as the amount of Phenol in the mixtures is reduced, the tendency for a greater selective adsorption of the caffein occurs at an ever widening range of applied polarisations. The (b) curves (Figs. 8, 9 and 10) show the same tendency for increased selective adsorption of Phenol as the amount of caffein is reduced. Since caffein is much less soluble than phenol as large a range of concentrations could not be employed and further the effects of electrocapillary viscosity, especially on the negative side of the adsorption curves, becomes very marked and make the measurements extremely difficult.

THEORETICAL.

Dr J.A.V. Butler has shown (private communication) how an empirical equation obtained by Szyskowski (Zeit. Phys. Chem. 1908, 64, 385), for the surface tension lowering caused by a solute in aqueous solution, may be developed to apply to a mixture containing two active solutes.

The Szyskowski equation is

$$\gamma = \gamma_0 - b\gamma_0 \log\left(\frac{x}{a} + 1\right) \qquad (1)$$

$$= \gamma_0 - b\gamma_0 \log(x+a) - b\gamma_0 \log a \qquad (2)$$

where/

where γ = surface tension of the solution, γ_0 = surface tension of the pure solvent, x = concentration of solute in gram moles per litre of solution and b and a are constants.

Inserting the value of $d\gamma$ obtained by differentiating (2), in the well known Gibbs' equation.

$$\Gamma = -\frac{d\gamma}{RT\, d\log x}$$

$$= \frac{1}{RT} \cdot \gamma_0 b \frac{x}{x+a} \qquad (3)$$

$$\left\{ \text{since } d\log(x+a) = \frac{1}{x+a} \cdot dx = \frac{x}{x+a} d\log x \right\}$$

KINETIC TREATMENT.

If A is the area of surface occupied by an adsorbed molecule and Γ the amount adsorbed then the total area of surface occupied $= A\Gamma$ per centimetre of surface and the unoccupied area $= 1 - A\Gamma$. The condition for equilibrium between rate of adsorption and rate of desorption is

$$x(1 - A\Gamma) = k\Gamma$$

where k is the equilibrium constant.

$$\therefore \quad x = Ax\Gamma + k\Gamma$$

$$\text{and} \quad \Gamma = \frac{x}{Ax + k} \qquad \frac{1}{A} \cdot \frac{x}{x + k/A} \qquad (3a)$$

which is equivalent to the deduction from the Szyskowski equation (3). Therefore combining (3) and (3a)

$$\frac{1}{A} = \frac{1}{RT} V_0 b \qquad (4)$$

$$\text{or} \quad a = \frac{k}{A} \qquad (4a)$$

Adsorption in Mixtures.

For two components.

$$k_1 \Gamma_1 = c_1(1 - A_1\Gamma_1 - A_2\Gamma_2) \qquad (5)$$

which is the equilibrium equation for the first component, and

$$k_2 \Gamma_2 = c_2(1 - A_1\Gamma_1 - A_2\Gamma_2) \qquad (6)$$

for the second component, where C_1 and C_2 are the concentrations

$$\frac{\Gamma_1}{\Gamma_2} = \frac{k_2}{k_1} \cdot \frac{c_1}{c_2} \qquad (7)$$

substituting in (5) the value of Γ_2 obtained in (7)

$$k_1\Gamma_1 = c_1(1 - A_1\Gamma_1 - A_2 k_1/k_2 \cdot c_2/c_1 \Gamma_1)$$

$$\text{or} \quad k_1\Gamma_1 + c_1 A_1 \Gamma_1 + k_2/k_1 A_2 c_2 \Gamma_1 = c_1$$

$$\therefore \quad \Gamma_1 = \frac{c_1}{k_1 + c_1 A_1 + k_1/k_2 A_2 c_2} \qquad (8)$$

For Mixtures of Two Components in which C_2 is constant.

Converting to surface tensions

$$(\Delta\gamma_1)_{c_2} = KT\int \Gamma_1 \, d\log c_1 = KT\int \frac{\Gamma_1}{c_1}\, dc_1$$

$$= KT\int \frac{1}{k_1 + c_1 A_1 + k_1/k_2 A_2 c_2} \cdot dc_1$$

obtained by substituting for Γ_1 , obtained in (8)

$$= \frac{KT}{A_1} \log \frac{k_1 + k_1/k_2 A_2 c_2 + A_1 c_1}{k_1 + k_1/k_2 A_2 c_2}$$

$$= \frac{KT}{A_1} \log \left\{ 1 + \frac{A_1}{k_1 (1 + A_2 c_2/k_2)} \cdot c_1 \right\}$$

$$= \frac{KT}{A_1} \log \left\{ 1 + \frac{c_1}{a_1 (1 + c_2/a_2)} \right\} \qquad (9)$$

by substituting for $A/k = a$ from (4a).

And when C_1 is small

$$(\Delta\gamma_1)_{c_2} = \frac{KT}{A_1} \cdot \frac{c_1}{a_1 (1 + c_2/a_2)} \qquad (9a)$$

and for $C_2 = 0$

$$(\Delta\gamma_1)_0 = \frac{KT}{A_1} \cdot \frac{c_1}{a_1} \qquad (10)$$

For C_2 alone when no other component is present from (9)

$$\Delta\gamma_{c_2} = \frac{KT}{A_2} \log (1 + c_2/a_2) \qquad (11)$$

$$\therefore \frac{(\Delta\gamma_1)_{c_2}}{(\Delta\gamma_1)_0} = \frac{1}{1 + c_2/a_2}$$

$$\text{or } \log \left\{ \frac{(\Delta\gamma_1)_{c_2}}{(\Delta\gamma_1)_0} \right\} = -\log (1 + c_2/a_2)$$

$$= -\Delta\gamma_{c_2} \frac{A_2}{KT} \qquad (12)$$

from (11)

$$\text{or} \quad \log (\Delta\gamma_1)_{c_2} = \log (\Delta\gamma_1)_0 - \Delta\gamma_{c_2} k' \qquad (13)$$

$$\therefore \quad k' = - \log \left\{ \frac{(\Delta\gamma_1)_{c_2}}{(\Delta\gamma_1)_0} \right\} \Big/ \Delta\gamma_{c_2} \qquad (14)$$

where k^1 is a constant.

According to equation (12), the logarithm of the ratio of the surface tension lowering produced by a component A_1 in a mixture containing components A_1 and A_2, to that produced by A_1 separately is proportional to the lowering produced by the second component separately.

Application of the Theory.

The equations may be applied to the surface tension lowerings produced by caffein on phenol solutions of different concentrations.

Thus

$$\log \left\{ \frac{(\Delta\gamma_c)_b}{(\Delta\gamma_c)_0} \right\} = - \Delta\gamma_b k'$$

where $(\Delta\gamma_c)_b$ = surface tension lowering produced by the addition of M/100 caffein to phenol, $(\Delta\gamma_c)_0$ = lowering produced by M/100 caffein alone and $\Delta\gamma_b$ = lowering produced by phenol alone.

Table/

Table I gives the values of these quantities for the potential differences V = -0.3, -0.5 and -0.7 volts respectively.

TABLE I.

V = -0.3. Caffein = M/100.

Phenol	$(\Delta\gamma_c)_b$	$(\Delta\gamma_c)_o$	$\log 10 \left\{\frac{(\Delta\gamma_c)_b}{(\Delta\gamma_c)_o}\right\}$	$\Delta\gamma_b$
M/10	1.2	7.3	.785	9.9
M/20	1.3	7.3	.748	8.2
M/50	2.0	7.3	.556	6.2
M/100	2.6	7.3	.447	5.0
M/200	3.2	7.3	.362	4.1

V = -0.5 Caffein = M/100

Phenol	$(\Delta\gamma_c)_b$	$(\Delta\gamma_c)_o$	$\log 10 \left\{\frac{(\Delta\gamma_c)_b}{(\Delta\gamma_c)_o}\right\}$	$\Delta\gamma_b$
M/10	2.0	8.7	.638	9.3
M/20	2.2	8.7	.597	7.6
M/150	3.5	8.7	.40	5.7
M/100	4.4	8.7	.295	4.4
M/200	5.0	8.7	.241	3.6

V = -0.7 Caffein = M/100.

Phenol	$(\Delta\gamma_c)_b$	$(\Delta\gamma_c)_o$	$\log 10 \left\{\frac{(\Delta\gamma_c)_b}{(\Delta\gamma_c)_o}\right\}$	$\Delta\gamma_b$
M/10	2.5	8.3	.521	7.6
M/20	3.0	8.3	.443	5.8
M/50	4.9	8.3	.225	3.8
M/100	5.9	8.3	.146	2.4
M/200	6.5	8.3	.107	1.8

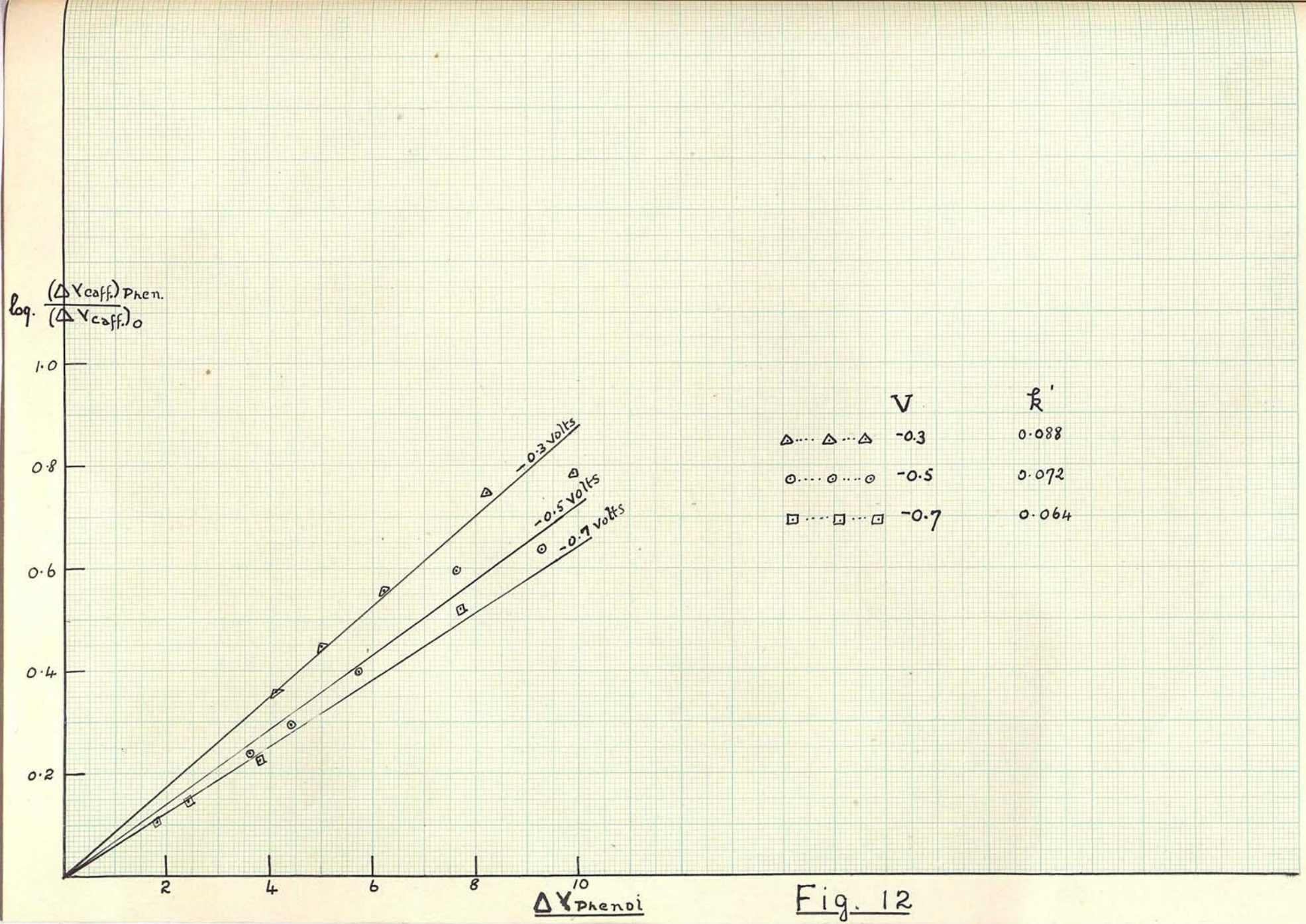
log. (ΔY caff.) Phen. / (ΔY caff.)₀
1·0
0·8
0·6
0·4
0·2
2
4
6
8
10
ΔY Phenol
-0·3 volts
-0·5 volts
-0·7 volts
V
k'
-0.3
0·088
-0.5
0·072
-0.7
0·064

Fig. 12

In Fig.12 values of $\log_{10}\left\{\frac{(\Delta\gamma_c)_b}{(\Delta\gamma_c)_o}\right\}$ are plotted against corresponding values of $\Delta\gamma_b$. It can be seen that a reasonably linear relation is obtained for each value of V. The value of k^1 (obtained from the slopes) should according to the theory be proportional to A_2 and should therefore be the same in each case: Actually the slopes are somewhat different. The mean values of k^1 are

V	k^1
-0.3	0.088
-0.5	0.072
-0.7	0.064

The effect on the equation of varying the potential difference at the interface has not been completely elucidated; possibly it is too severe a test to expect the theory to apply at varying potentials. It is evident that it applies reasonably well at constant V.

A sufficiently great range of caffein concentrations is not available in order to apply the same relation to the effect of phenol on caffein solutions.

Similar calculations have been made of the effect produced by M/20 sodium o-toluate on solutions of sodium cinnamate (Mixtures 4, 5 and 6) at various potentials. All the points for V = -0.1, -0.3, -0.5, -0.7 and -0.9 volts are given in Fig. 13.

An/

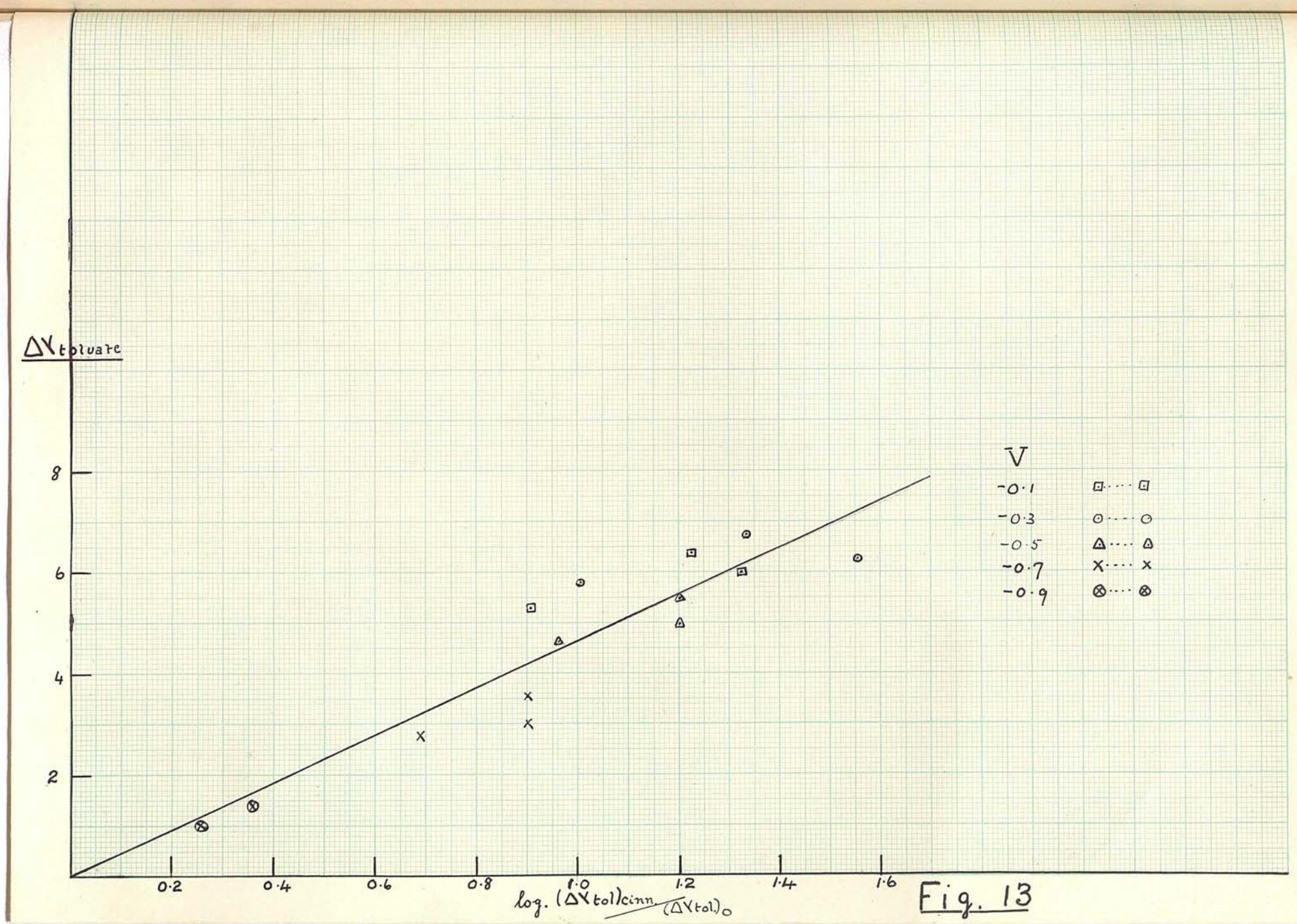
ΔY totuate
8
6
4
2
0·2
0·4
0·6
0·8
1·0
1·2
1·4
1·6
log. (ΔY tol)cinn / (ΔY tol.)o
V
-0·1
-0·3
-0·5
-0·7
-0·9

Fig. 13

An approximately linear relation appears. In these solutions the lowering of the surface tension produced by sodium o-toluate is, with a few exceptions, only about twice the experimental error and taking this into consideration the agreement is considered satisfactory. The mean value of k^1 is 0.217.

The lowerings produced by sodium o-toluate in stronger solutions, which were found to be within the experimental error, can be calculated by equation(13), using the mean value of k^1. It appears that in M/50 sodium cinnamate (mixture 3) the effect of M/20 sodium o-toluate while small, should still be observable. It thus appears that the rate at which the effect of the toluate disappears is greater than predicted by the equation. This may be due to some additional term required in Szyskowski's equation for adsorbed ions.

It can easily be shown that the equation is able to account for cases of complete "selection" observed in other cases. For example in the salicin - saccharose mixture, at -1.35 volts a value of .375 is obtained for k^1. Using this value to calculate the lowering expected at -0.5 volts it is found that ($\Delta\gamma$ Sacc.) sal.- the lowering produced by M/20 saccharose in the mixture - is 0.00214 cms. Actually no lowering was observed; the calculated lowering is also much too small to be observed.

When/

When applied to the Phenol-lactose mixture (Part II) the value of k^1 obtained at -1.0 volts is .35. The calculated lowering produced by M/20 lactose at -0.4 volts in the mixture is 0.0063 units on the Gouy scale. Here no lowering was observed and the calculated lowering is also much too small to be observed.

The theory when applied to the caffein-lactose mixture (Part II) gives a value for k^1 at -1.3 volts of .61. The calculated lowering produced by M/20 lactose at -0.5 volts is 0.000024 units on the Gouy scale. Here also no lowering was observed, the calculated lowering being also much too small to be observed.

It must be remembered that all the solutions contained M/2 sodium sulphate and this component has not been considered in the theory. As far as present observations go the equations given apply reasonably adequately, but a study of more systems is required to establish it on a firm basis.

TABLE II.

V.	Sodium Sulphate M/2	Sodium o-toluate M/20	Sodium Cinnamate M/20	Sod. Cinnamate M/20 and Sod. o-toluate M/20	Sodium Cinnamate M/40
+ 0.1	44.56	43.74	42.10	42.10	42.58
0.0	47.20	45.53	43.87	43.88	44.27
- 0.1	49.15	47.02	45.28	45.28	45.61
- 0.2	50.47	48.24	46.39	46.45	46.75
- 0.3	51.39	49.21	47.32	47.38	47.68
- 0.4	51.81	49.89	48.06	48.04	48.40
- 0.5	51.93	50.31	48.46	48.48	48.78
- 0.6	51.71	50.47	48.76	48.79	48.96
- 0.7	51.18	50.33	48.80	48.86	49.05
- 0.8	50.37	49.88	48.66	48.66	48.90
- 0.9	49.35	49.12	48.16	48.21	48.44
- 1.0	48.14	48.06	47.44	47.47	47.62
- 1.1	46.68	46.65	46.34	46.38	46.47
- 1.2	45.04	45.07	44.95	44.98	44.98
- 1.3	43.22	43.22	43.17	43.21	43.20
- 1.4	41.23	41.24	41.18	41.20	41.22
- 1.5	38.98	38.96	38.96	38.98	38.97
- 1.6	36.51	36.55	36.46	36.50	36.48
- 1.7	33.87	33.88	33.84	33.88	33.82
- 1.8	30.96	30.98	30.96	30.91	30.94
- 1.9	27.78	27.81	27.76	27.80	27.80
- 2.0	24.37	24.38	24.32	24.34	24.35

V.	Sod. Cinna. M/40 and Sod. o-Toluate M/20	Sodium Cinnamate M/50	Sod.Cinna. M/50 and Sod. o-Toluate M/20	Sodium Cinnamate M/60	Sod. Cinna. M/60 and Sodium o-Toluate M/20
0.1	42.51	42.74	42.70	42.82	42.68
0.0	44.24	44.47	44.42	44.61	44.40
0.1	45.62	45.93	45.84	45.94	45.79
0.2	46.75	46.93	46.94	47.04	46.96
0.3	47.69	47.88	47.89	48.02	47.88
0.4	48.36	48.57	48.59	48.71	48.61
0.5	48.77	49.05	49.07	49.12	49.06
0.6	48.98	49.27	49.27	49.46	49.36
0.7	49.05	49.30	49.30	49.43	49.34
0.8	48.89	49.08	49.09	49.21	49.08
0.9	48.42	48.57	48.57	48.66	48.54
1.0	47.59	47.73	47.76	47.78	47.68
1.1	46.46	46.50	46.52	46.57	46.51
1.2	44.98	45.02	45.03	45.05	45.02
1.3	43.22	43.14	43.12	43.23	43.21
1.4	41.23	41.15	41.17	41.18	41.20
1.5	38.96	39.96	38.94	38.96	38.93
1.6	36.48	36.50	36.52	36.54	36.56
1.7	33.84	33.84	34.87	33.86	33.88
1.8	30.85	30.95	30.93	30.95	30.92
1.9	27.78	27.76	27.80	27.79	27.76
2.0	24.36	24.35	24.33	24.63	24.67

V.	Sodium Cinnamate M/100	Sod. Cinna. M/100 and Sod. o-toluate M/20	Sodium Cinnamate M/150	Sod. Cinna. M/150 and Sod. o-Toluate M/20	Sodium Cinnamate M/300
0.1	43.13	43.01	43.62	43.17	43.86
0.0	44.76	44.66	45.22	44.80	45.67
0.1	46.17	46.03	46.49	46.26	46.94
0.2	47.28	47.17	47.58	47.38	47.97
0.3	48.25	48.10	48.47	48.28	48.85
0.4	48.96	48.80	49.14	48.98	49.49
0.5	49.45	49.30	49.60	49.46	49.87
0.6	49.66	49.55	49.80	49.65	50.08
0.7	49.67	49.51	49.77	49.62	50.03
0.8	49.41	49.28	49.53	49.39	49.77
0.9	48.84	48.71	48.94	48.81	49.21
1.0	47.87	47.73	47.95	47.87	48.01
1.1	46.59	46.50	46.61	46.61	46.64
1.2	45.04	44.96	45.05	45.04	45.06
1.3	43.21	43.17	43.20	43.22	43.20
1.4	41.20	41.17	41.22	41.18	41.24
1.5	38.94	38.96	38.91	38.94	38.99
1.6	36.52	36.48	36.49	36.51	36.54
1.7	33.82	33.82	33.87	33.86	33.86
1.8	30.96	30.92	30.95	30.94	30.94
1.9	27.75	27.78	27.79	27.78	27.80
2.0	24.35	24.32	24.33	24.35	24.36

TABLE III.

V.	Phenol M/10	Caffein M/100	Phenol M/10 and Caffein M/100	Phenol M/20	Phenol M/20 and Caffein M/100
0.1	42.96	44.74	42.97	43.39	43.38
0.0	44.18	46.73	44.08	44.88	44.63
0.1	45.06	47.39	44.61	45.78	45.45
0.2	45.84	47.51	45.28	46.63	46.17
0.3	46.46	47.71	45.88	47.29	46.66
0.4	46.97	47.67	46.17	47.77	46.88
0.5	47.26	47.56	46.26	48.11	46.97
0.6	47.34	47.28	46.26	48.27	46.91
0.7	47.37	47.01	46.18	48.29	46.76
0.8	47.27	46.60	45.90	48.15	46.34
0.9	46.98	46.19	45.48	47.90	45.99
1.0	46.60	45.57	45.07	47.41	45.48
1.1	45.93	44.87	44.56	46.37	44.88
1.2	44.83	44.24	44.26	44.97	44.21
1.3	43.17	42.78	42.95	43.27	42.78
1.4	41.22	40.96	41.00	41.24	40.95
1.5	39.02	38.87	38.88	38.96	38.86
1.6	36.62	36.51	36.51	36.50	36.49
1.7	34.00	33.87	33.99	33.86	33.87
1.8	31.09	30.94	31.06	30.93	30.94
1.9	27.99	27.79	27.97	27.76	27.76
2.0	24.60	24.36	24.53	24.34	24.33

V.	Phenol M/50	Phenol M/50 and Caffein M/100	Phenol M/100	Phenol M/100 and Caffein M/100	Phenol M/200
+ 0.1	44.02	43.99	44.30	44.28	44.58
0.0	45.74	44.52	46.10	45.70	46.57
- 0.1	46.80	46.28	47.21	46.66	47.71
- 0.2	47.69	46.87	48.16	47.22	48.60
- 0.3	48.27	47.27	48.88	47.53	49.33
- 0.4	48.71	47.35	49.37	47.58	49.81
- 0.5	49.07	47.31	49.73	47.51	50.10
- 0.6	49.24	47.10	50.83	47.31	50.31
- 0.7	49.28	46.80	49.97	47.00	50.28
- 0.8	49.17	46.52	49.82	46.63	49.97
- 0.9	48.76	46.03	49.08	46.00	49.17
- 1.0	47.90	45.57	48.01	45.56	48.06
- 1.1	46.61	44.90	46.68	44.96	46.66
- 1.2	45.07	44.32	45.08	44.26	45.06
- 1.3	43.21	42.93	43.26	42.96	43.25
- 1.4	41.22	40.98	41.27	40.99	41.24
- 1.5	38.95	38.87	39.07	38.87	39.00
- 1.6	36.48	36.54	36.65	36.50	36.56
- 1.7	33.83	33.94	34.97	33.89	33.88
- 1.8	30.94	31.02	31.08	30.99	30.99
- 1.9	27.80	27.88	27.97	27.85	27.85
- 2.0	24.34	24.48	24.58	24.42	24.42

V.	Phenol M/200 and Caffein M/100	Caffein M/50	Caffein M/50 and Phenol M/20	Caffein M/300	Caffein M/300 and Phenol M/20
+ 0.1	44.59	44.67	43.35	44.61	43.39
0.0	46.30	46.47	44.60	47.08	44.86
- 0.1	46.95	46.98	45.27	47.93	45.74
- 0.2	47.43	47.21	45.94	48.19	46.48
- 0.3	47.65	47.31	46.36	48.30	46.98
- 0.4	47.66	47.26	46.51	48.28	47.26
- 0.5	47.55	47.11	46.57	48.15	47.35
-0.6	47.29	46.91	46.47	48.97	47.31
- 0.7	46.98	46.58	46.21	47.58	47.08
- 0.8	46.60	46.15	45.89	47.27	46.85
- 0.9	46.18	45.63	45.46	46.77	46.46
- 1.0	45.55	45.05	44.88	46.27	46.17
- 1.1	44.87	44.31	44.26	45.82	45.77
- 1.2	44.28	43.48	43.44	44.88	44.87
- 1.3	42.79	42.18	42.20	43.12	43.12
- 1.4	40.97	40.67	40.64	41.12	41.08
- 1.5	38.85	38.71	38.70	38.96	38.95
- 1.6	36.48	36.41	36.42	36.54	36.52
- 1.7	33.88	33.84	33.84	33.87	33.90
- 1.8	30.98	30.95	30.98	30.94	31.00
- 1.9	27.83	27.78	27.79	27.78	27.88
- 2.0	24.40	24.37	24.36	24.35	24.46

TABLE IV.

V.	Saccharose M/2	Salicin M/20	Salicin M/20 and Saccharose M/2
+ 0.1	44.30	43.76	43.56
- 0.0	46.31	45.45	45.31
- 0.1	47.79	46.54	46.46
- 0.2	48.75	47.26	47.18
- 0.3	49.29	47.61	47.60
- 0.4	49.51	47.83	47.82
- 0.5	49.53	47.90	47.87
- 0.6	49.35	47.81	47.81
- 0.7	48.99	47.58	47.55
- 0.8	48.44	47.21	47.20
- 0.9	47.73	46.70	46.65
- 1.0	46.81	46.04	45.95
- 1.1	45.71	45.17	45.02
- 1.2	44.37	44.08	43.87
- 1.3	42.77	42.69	42.44
- 1.4	40.91	40.99	40.74
- 1.5	38.78	38.96	38.73
- 1.6	36.45	36.56	36.41
- 1.7	33.82	33.93	33.80
- 1.8	30.96	31.07	30.96
- 1.9	27.80	27.91	27.78
- 2.0	24.36	28.48	24.39

SUMMARY.

1. The electrocapillary curves of a number of aqueous solutions containing mixtures at various concentrations of two surface active substances have been determined. The electrocapillary curves of the separate components, at the same concentrations as in the mixtures, have also been determined.

2. Mixtures of a wide range of concentrations of sodium cinnamate and a constant amount of sodium o-toluate show that the effect of the latter component can be measured within a narrow range of concentrations of the former. In a mixture containing M/50 sodium cinnamate the effect on the surface tension lowering of the addition of M/20 sodium o-toluate is inappreciable, but with M/60 sodium cinnamate the effect becomes appreciable.

3. The adsorption curves of mixtures of Phenol-Caffein solutions indicate that as the Phenol concentration is reduced, the tendency for increased selective adsorption of the Caffein occurs at an ever widening range of applied potential differences. The same tendency is observed for Phenol as the concentration of caffein is reduced.

4./

4. With a mixture of salicin and saccharose a new type of selective adsorption is obtained; the effect of saccharose on the salicin adsorption curve being only appreciable at both extreme ends.

5. Equations developed from adsorption theory apply reasonably well to the observations made in the sodium cinnamate - sodium o-toluate mixtures, but indicate a greater effect for the surface tension lowering produced by the toluate than is actually observed.

6. The equations applied to cases of other mixtures indicate that practically complete selective adsorption of the more surface active component is to be expected. The surface tension lowering produced by the second component in these cases is not measurable, and this is adequately confirmed by the calculations.

It is with the utmost pleasure that I take this opportunity of expressing my deep indebtedness to Dr J.A.V. Butler for his generous advice and many valuable suggestions, and to Sir James Walker, V.P.R.S., for his kindly interest, throughout the course of this study.